

## Doctoral Thesis

# **The extension of Statistical Entropy Analysis to chemical compounds**

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## Abstract

Statistical Entropy Analysis (SEA) is a quantitative evaluation method that determines the extent of concentration respective, dilution of a substance caused by a process or system. SEA has been repeatedly used for the assessment of losses of heavy metals from waste treatment facilities leading to a better understanding of the significance of concentration processes for sustainable materials recycling. However, SEA is limited to applications to chemical elements, while the specification of an element is sometimes of particular importance. Therefore, in this work, SEA is extended to chemical compounds (extended SEA (eSEA)) and the benefits of eSEA are demonstrated based on two examples related to water resource systems, namely farming regions and wastewater treatment.

Chapter 1 gives an introduction to the doctoral thesis. The extension of SEA to chemical compounds is presented in Chapter 2 based on a system, consisting of a hypothetical crop farming region. Such a system primarily converts the nitrogen from different material flows such as fertilizer, seeds, and air to food products. However, various nitrogen compounds such as ammonium ( $\text{NH}_4^+$ ), nitrate ( $\text{NO}_3^-$ ), and organically bound nitrogen ( $\text{N}_{\text{org}}$ ) find their way into surface waters and into the groundwater, and compounds such as elemental nitrogen ( $\text{N}_2$ ), dinitrous oxide ( $\text{N}_2\text{O}$ ), ammonia ( $\text{NH}_3$ ), and other nitrous oxides ( $\text{NO}_x$ ) are lost to the atmosphere during this process. SEA makes no difference between the emission of  $\text{N}_2$ ,  $\text{N}_2\text{O}$  and  $\text{NH}_3$  or between  $\text{NH}_4^+$  and  $\text{NO}_3^-$  although their impact on the environment differs considerably. This limitation can be overcome by using eSEA. All nitrogen compounds, which are released into the different environmental compartments such as groundwater, surface water and the atmosphere, are differentiated thus providing a more precise evaluation of the nitrogen losses of the particular crop farming region. The extent to which the region dilutes nitrogen compounds is expressed as the change in statistical entropy ( $\Delta H$ ). Four variations of the crop farming system are tested, showing that the efficiency of crop farming can be expressed by eSEA.

In Chapter 3, eSEA is used to evaluate the nitrogen budgets of two Austrian catchments, the Wulka and the Ybbs, and of entire Austria. The results obtained by eSEA are compared to the particular nitrogen-use-efficiencies (NUEs) and discussed in the context of suitability for evaluation of the nitrogen performance of the regions. The eSEA enables quantification of the extent of nitrogen dilution based on the

consideration of all types of nitrogen compounds and of the distribution of these compounds in various material flows and is thus a more comprehensive method for the assessment of the nitrogen performance of agricultural systems than the NUE. According to eSEA the nitrogen management of the Wulka catchment is more favorable than that of the Ybbs catchment because it dilutes less nitrogen in the environment. The NUE of the Wulka catchment is also significantly higher than that of the Ybbs catchment. Based on eSEA, it is also demonstrated that a healthy, balanced diet, as defined by the German Nutrition Society, interferes in the Austrian nitrogen budget in a way that significantly reduces the dilution of nitrogen. The national NUE of Austria however increases only marginally. Furthermore, if uncertainty of the input data is taken into account the NUE becomes insignificant.

In Chapter 4, eSEA is used to assess the nitrogen removal performance of 56 Austrian wastewater treatment plants (WWTPs). The reduction in statistical entropy,  $\Delta H$ , expresses the nitrogen removal performance compared to a direct discharge of the particular wastewater to the river. The higher  $\Delta H$  is the more favorable is the nitrogen removal performance. The  $\Delta H$  values are compared to the corresponding nitrogen removal rates. Among 5 WWTPs that achieve a removal rate of 75% the eSEA detects significant differences in the nitrogen removal performance. The eSEA differentiates all the nitrogen compounds that occur after WWT and their distribution in the receiving waters, the atmosphere, and the sludge, thus providing a more comprehensive assessment of the nitrogen removal performance of WWTPs. The eSEA results are furthermore related to economic factors such as the energy consumption and the total costs associated with the nitrogen treatment. It results that energy-efficient nitrogen treatment does not necessarily imply cost-effectiveness and that small WWTPs, per definition those responsible for pollution loads less than 50,000 population equivalents (PE) can operate as energy-efficient and at times, even likewise cost-effective as large WWTPs that treat wastewaters with pollution loads higher than 50,000 PE. These results are in contrast to the literature findings, which state that large WWTPs are generally more energy-efficient and cost-effective.

Based on the benefits of eSEA for the assessment of the nitrogen removal performance of WWTPs derived in the previous chapter, eSEA is implemented into the traditional effluent quality index (EQ) of the Benchmarking Simulation Model (BSM) N°2. For this purpose, in Chapter 5, the traditional EQ is restructured to  $\Delta EQ_{new}$ .  $\Delta EQ_{new}$  is expressed in % as the weighted sum of the reduction in statistical entropy,

$\Delta H$ , and the removal rate of chemical and biological oxygen demand (COD, BOD), and suspended solids (SS) compared to a direct discharge of the particular wastewater to the river. Thus,  $\Delta EQ_{new}$  is a more comprehensive indicator than the traditional EQ providing information about the cleaning performance of a particular WWT system rather than just quantifying the effluent quality. Furthermore, it is found that the simulated  $N_2O$  emissions in the range of 0.34% to 0.44% relative to the total nitrogen in the wastewater have only a minor effect on the eSEA results, and consequently also on  $\Delta EQ_{new}$ .

Chapter 6 finally summarizes the findings of this doctoral thesis and derives the implications of this work. In addition, the advantages and disadvantages of eSEA are discussed with reference to the presented systems, namely farming regions and WWTPs.

## Kurzfassung

Die statistische Entropie Analyse (SEA) ist eine quantitative Methode zur Bewertung des Ausmaßes an Konzentration bzw. Verdünnung einer Substanz, die durch einen Prozess oder ein System verursacht wird. SEA wurde bisher mehrfach in der Bewertung von Müllverarbeitungsanlagen eingesetzt. Daraus hat man die Bedeutung von Konzentrierungsprozessen für ein nachhaltiges Stoffrecycling erkannt. Derzeit ist SEA auf Anwendungen für einzelne chemische Elemente beschränkt. In manchen Fällen ist es jedoch besonders wichtig, zu unterscheiden, in welcher chemischen Bindung ein Element vorliegt. Daher wird in dieser Arbeit die SEA auf chemische Verbindungen erweitert (erweiterte SEA (eSEA)). Der Nutzen der eSEA wird anhand zweier, für Wasserressourcen relevanter Systeme, nämlich landwirtschaftliche Regionen und Abwasserreinigungsanlagen veranschaulicht.

Das erste Kapitel besteht aus einer Einleitung zu der hier vorliegenden Dissertation. Die Erweiterung der SEA auf chemische Verbindungen wird anhand einer hypothetischen Region, in der Pflanzenbau betrieben wird, im zweiten Kapitel vorgestellt. In solch einer Region wird Stickstoff aus verschiedenen Materialflüssen wie zum Beispiel Dünger, Saatgut und Luft in pflanzliche Nahrungsmittel umgewandelt. Dabei gelangen unterschiedliche Stickstoffverbindungen wie Ammonium ( $\text{NH}_4^+$ ), Nitrat ( $\text{NO}_3^-$ ) und organisch gebundener Stickstoff ( $\text{N}_{\text{org}}$ ) in Oberflächengewässer und in das Grundwasser. Elementarer Stickstoff ( $\text{N}_2$ ), Lachgas ( $\text{N}_2\text{O}$ ), Ammoniak ( $\text{NH}_3$ ) und andere Stickoxide ( $\text{NO}_x$ ) werden währenddessen in verschiedenen Konzentrationen in die Atmosphäre ausgestoßen. Die SEA unterscheidet weder zwischen der Emission von  $\text{N}_2$ ,  $\text{N}_2\text{O}$  und  $\text{NH}_3$  noch zwischen der von  $\text{NH}_4^+$  und  $\text{NO}_3^-$ , obwohl sich die Auswirkungen der jeweiligen Stickstoffverbindungen auf die Umwelt deutlich voneinander unterscheiden. Dieser Nachteil kann durch den Einsatz der eSEA ausgeglichen werden. Alle Stickstoffverbindungen, die in die Umwelt gelangen, werden differenziert, wodurch eine präzisere Bewertung der Stickstoffverluste der Region gewährleistet wird. Das Ausmaß der Konzentrierung bzw. der Verdünnung der Stickstoffverbindungen wird als Änderung der statistischen Entropie ( $\Delta H$ ) ausgedrückt. Vier verschiedene Emissionsszenarien werden am Beispiel solch einer Region getestet. Es zeigt sich, dass die eSEA eine geeignete Bewertungsmethode zur Beurteilung der Stickstoffleistung einer Region darstellt.

Im dritten Kapitel wird der Stickstoffhaushalt zweier österreichischer Einzugsgebiete, Wulka und Ybbs, und der ganz Österreichs mithilfe von der eSEA bewertet. Die gewonnenen Ergebnisse werden mit den einzelnen Stickstoff-Nutzungseffizienzen (NUE) verglichen und in Hinsicht auf ihre Zweckmäßigkeit für die Bewertung der Stickstoffleistung der Regionen diskutiert. Die eSEA ermöglicht es, das Ausmaß der Stickstoffverdünnung zu quantifizieren und dabei alle Stickstoffverbindungen samt ihrer Verteilung in den einzelnen Materialflüssen zu berücksichtigen. Sie stellt somit eine umfassendere Methode zur Bewertung der Stickstoffleistung landwirtschaftlicher Regionen dar als die NUE. Laut eSEA ist der Stickstoffhaushalt des Wulka Einzugsgebietes dem des Ybbs Einzugsgebiets zu bevorzugen, weil durch die Bewirtschaftung insgesamt weniger Stickstoff in die Umwelt verloren geht. Die NUE des Wulka Einzugsgebiets ist ebenfalls deutlich höher als die des Ybbs Einzugsgebiets. Die eSEA zeigt weiterhin, dass eine gesunde Ernährungsweise, wie sie von der Deutschen Gesellschaft für Ernährung empfohlen wird, sich derart auf den Stickstoffhaushalt Österreichs auswirkt, dass deutlich weniger Stickstoffverluste in die Umwelt auftreten. Die NUE Österreichs erhöht sich jedoch nur gering. Ferner geht der Unterschied in den NUE zwischen der gängigen und der optimierten Ernährungsweise Österreichs gänzlich verloren, sobald die Unsicherheiten der Daten mit einberechnet werden.

Im vierten Kapitel wird die eSEA dazu verwendet, um die Stickstoffentfernungsleistung von 56 österreichischen Kläranlagen zu bewerten. Die Abnahme in der statistischen Entropie,  $\Delta H$ , wird zum Maß für die Stickstoffentfernungsleistung, verglichen mit der direkten Einleitung des unbehandelten Abwassers in den Fluss. Je höher  $\Delta H$  ist, desto größer ist auch die Stickstoffentfernungsleistung. Die  $\Delta H$  Werte werden mit den jeweiligen Stickstoffentfernungsraten verglichen. Dabei zeigen fünf Kläranlagen, die exakt 75% des Gesamtstickstoffs aus dem Abwasser entfernen, unterschiedliche Stickstoffentfernungsleistungen, wenn diese mithilfe der eSEA bewertet werden. Die eSEA unterscheidet alle Stickstoffverbindungen, die vor und nach der Abwasserreinigung entstehen und berücksichtigt auch ihre Verteilung im Ablauf, im Abgas und im Schlamm. Dadurch wird eine umfassendere Bewertung der Stickstoffentfernungsleistung der jeweiligen Kläranlagen ermöglicht. Die Ergebnisse aus der eSEA werden zusätzlich noch zu ökonomischen Faktoren wie dem Energieverbrauch und der Kosten in Verhältnis gesetzt. Daraus ergibt sich, dass eine energieeffiziente Stickstoffentfernung nicht notwendigerweise auch Kosteneffizienz impliziert. Kleine Kläranlagen, die für Schmutzfrachten weniger als 50,000

Einwohnerwerte (EW) verantwortlich sind, können ebenso energieeffizient und teilweise auch gleichermaßen kosteneffektiv betrieben werden wie große Kläranlagen, die Schmutzfrachten größer als 50,000 EW behandeln. Diese Ergebnisse widersprechen denen aus der gängigen Literatur, die besagen, dass große Kläranlagen grundsätzlich energieeffizienter und kosteneffektiver arbeiten.

Ausgehend von den Vorzügen der eSEA für die Bewertung der Stickstoffentfernungsleistung von Kläranlagen, die im vorhergehenden Kapitel erschlossen wurden, wird im fünften Kapitel die eSEA in den Ablaufqualitätsindex (EQ) der Abwasserreinigung simulierenden Software Benchmarking Simulation Model (BSM) N°2 integriert. Hierzu wird der EQ zu  $\Delta EQ_{new}$  umstrukturiert.  $\Delta EQ_{new}$  bildet die gewichtete Summe aus der Abnahme in der statistischen Entropie,  $\Delta H$  und der Entfernungsrates für den chemischen und biologischen Sauerstoffbedarf (COD, BOD) sowie für Schwebestoffe (SS), verglichen mit der direkten Einleitung des unbehandelten Abwassers in den Fluss und wird in % ausgedrückt.  $\Delta EQ_{new}$  ist somit ein umfassenderer Indikator als der für gewöhnlich verwendete Indikator EQ, da er die gesamte Reinigungsleistung der Kläranlage bewertet und nicht nur die Ablaufqualität. Die simulierten  $N_2O$  Emissionen bewegen sich in der Größenordnung zwischen 0.34% und 0.44% bezogen auf den Gesamtstickstoff im Abwasser und es zeigt sich, dass  $N_2O$  Emissionen in dieser Höhe lediglich einen kleinen Effekt auf die eSEA Ergebnisse und somit auch auf  $EQ_{new}$  haben.

Im sechsten Kapitel werden schließlich die Ergebnisse dieser Dissertation zusammengefasst und die Folgerungen aus dieser Arbeit dargestellt. Zudem werden die Stärken und Schwächen der eSEA für die Bewertung der hier vorgestellten Systeme diskutiert.

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# 1 Introduction

Despite of persistent research on water resources, still only little is known about the losses of substances from technological material cycles to the environment, many of which are linked to the presence and or flow of water. Obvious interactions exist between non-water material flows and the flow of water, for example, through the pollution of water bodies by heavy metals. In resource management, considerable progress has been made in recent years in the analysis and description of anthropogenic systems but the problem of resource evaluation is still not solved. Specifically, it is unclear how to evaluate the exploitation and use of resources, and how to evaluate the environmental impact of resource consumption. Current evaluation practice is dominated by Life Cycle Impact Assessment (LCIA), the value of which is undisputed. While LCIA is based on cause-and-effect relationships it cannot describe well processes such as dilution, dissipation or deterioration of substances and materials.

The proposed dissertation will make a contribution to the development of a metric for quantifying and assessing dissipation and devaluation phenomena of materials. The new method will be applied to nitrogen budgets in agricultural processes and waste water treatment plants (WWTPs). This will result in a better understanding of the characteristics and relevance of nitrogen emissions and losses from the anthroposphere.

Nitrogen is one of the important limiting nutrients of terrestrial, freshwater, and marine ecosystems (Tilman, et al., 1982), (Vitousek, 1982), (Socolow, 1999). A surplus of nitrogen will, however have a deteriorating effect on the environment. This includes eutrophication and acidification of water bodies, contribution to the greenhouse gas effect and photochemical oxidation. For a precise assessment of the environmental impact of nitrogen losses, it is crucial to distinguish how the nitrogen is chemically bound. A certain quantity of ammonium-nitrogen ( $\text{N-NH}_4^+$ ) will, for example, make a greater contribution to eutrophication than the same amount of nitrate-nitrogen ( $\text{N-NO}_3^-$ ), (Heijungs, et al., 1992), (Goedkoop & Spriensma, 2001), (Guinée, et al., 2002), (Pennington, et al., 2005), (Pennington, et al., 2006). For this reason, emission limits for  $\text{NH}_4^+$  and  $\text{NO}_3^-$  differ considerably (BGBI II Nr, 98/2010), (BGBI II Nr, 461/2010). Aquatic eutrophication, in turn, can lead to a loss of biodiversity, outbreak of nuisance species, shifts in the structure of food chains and impairment of fisheries

(Tilman, 1999). In addition, nitrogen compounds such as  $\text{NO}_3^-$  and nitrite ( $\text{NO}_2^-$ ) show a direct toxicological effect on water organisms and humans whereat the harming potential of  $\text{NO}_2^-$  is, in average, one to two orders of magnitude higher than that of  $\text{NO}_3^-$  (Korwin-Kossakowski, et al., 1995), (98/83/EC, 1998), (Camargo & Alonso, 2006), (EPA, 2007), (Speijers & Fawell, 2011). Nitrous oxide ( $\text{N}_2\text{O}$ ) is, amongst others, generated during wastewater treatment and agricultural production and has a greenhouse gas effect that is 296 times higher than that of  $\text{CO}_2$  (Ehhalt & Prather, 2001). Nitric oxide ( $\text{NO}$ ) and nitrogen dioxide ( $\text{NO}_2$ ), in turn, cause photochemical oxidation, which leads to elevated concentrations of ozone ( $\text{O}_3$ ), a gas that is toxic to both plants and humans (Fuhrer, 1994), (Ashmore, 2002), (Long & Naidu, 2002). Ammonia ( $\text{NH}_3$ ),  $\text{NO}$ ,  $\text{NO}_2$ , and  $\text{NO}_x$  have a negative effect on the respiratory system of mammals and are also known to cause terrestrial acidification (Vines & Wedding, 1960), (Burns, et al., 1985), (Bouwman & van Vuuren, 1999), (Ip, et al., 2001), (Frampton, et al., 2002), (Ricciardolo, et al., 2004). The pollution of terrestrial ecosystems with nitrogen is particularly critical because the lifetime of the nitrogen can extend to a few decades thus providing opportunities for transport of nitrogen into freshwater or the atmosphere (Fowler, et al., 2013). In addition to the effects of individual nitrogen compounds on the environment, the nitrogen cycle interferes with the carbon- and the phosphorus cycle and, in consequence, plays a role in climate change (Gruber & Galloway, 2008). Climate change, in turn, affects the global food production, amongst others. Due to altered temperature trends, the median global yield decreased by 3.1% for maize and by 4.9% for wheat between 1980 and 2008 (Lobell, et al., 2011). Another consequence of altered temperature trends is increasing emission of  $\text{NH}_3$ . 5°C warming can correspond to an additional emission of  $\text{NH}_3$  in the range of 28% to 67% (Sutton, et al., 2011). The nitrogen cycle is strongly influenced by the anthroposphere. This is indicated i.a., by the correlation of  $\text{NO}_3^-$  concentrations in the large rivers of the world and human population densities in the watersheds (Cole, et al., 1993). The biggest anthropogenic nitrogen input by far comes from agriculture. Approximately 58% of the total world-wide inorganic nitrogen transport results from fertilizers while human sewage accounts for 24% and deposition for 18% (Bouwman & van Vuuren, 1999). Growing global food production implies an additional increase in the nitrogen fertilization rate. The world-wide food demand is expected to increase by 70% to 100% until 2050 (Harrison, et al., 2002), (De Fraiture & Wichelns, 2007), (WWAP, 2012). Doubling the global food production, however, would triple the annual rate of nitrogen release (Tilman, 1999). One possibility to effectively reduce the



negative impact of agriculture on the environment is, for example, a change in human diet. It was found that a healthy, balanced diet can be secured while, at the same time, nitrogen emissions to the environment can be reduced (Stehfest, et al., 2009), (Fazeni & Steinmüller, 2011), (Sutton, et al., 2011), (Godfray, et al., 2010), (Thaler, 2009).

Wastewater treatment (WWT) is one of the three main contributors to the global environmental load along the whole anthropogenic water cycle (Lassaux, et al., 2007). The main aim of WWT is the removal of nutrients and pathogens from the wastewater for the purpose of water reuse and protection of the receiving waters. Nutrients are typically characterized by the chemical and biological oxygen demand (COD, BOD), Kjeldahl- nitrogen ( $\text{TKN}=\text{NH}_4^++\text{N}_{\text{org}}$ ), and phosphorus. Pathogens are typically removed with the help of disinfection processes. However, they can also be attached to the suspended solids (SS). Therefore, SS also need to be removed from the wastewater for the most part. Organic carbon compounds, nitrogen, and parts of phosphorus are broken down by bacteria under aerobic and anaerobic conditions. The bacteria are then transferred to the sludge while end products such as  $\text{CO}_2$  and  $\text{N}_2$  are emitted to the atmosphere. Phosphorus is additionally removed by chemical precipitation. After the biological treatment residual amounts of  $\text{N}_{\text{org}}$  and  $\text{NH}_4^+$  will still be found in the effluent together with the nitrification products  $\text{NO}_3^-$  and  $\text{NO}_2^-$  (Martin, 1927). Emission of the nitrification and denitrification by-product  $\text{N}_2\text{O}$  is hardly evitable, either (Kampschreur, et al., 2007). The mandatory extent of the removal of nutrients and pathogens is reported in the European Urban Wastewater Treatment Directive, for instance (91/271/EEC, 1991). In addition, Austrian standards require a plant size-specific nitrogen removal rate of more than 70%, at temperatures  $> 12\text{ }^\circ\text{C}$  for all treatment plants with more than 5,000 population equivalents (PE) and an  $\text{NH}_4^+$  concentration below 10 mg(N)/L and 5 mg(N)/L for plants with more than 500 PE respectively (Philippitsch & Grath, 2006). Most wastewater treatment plants (WWTPs) on average comply with such mandatory requirements but the performance can still highly vary on seasonal and even daily basis. Treatment and discharge systems can also sharply differ between countries and between rural and urban areas, with respect to urban high income and urban low-income users even in developed nations (Doorn, et al., 2006). In addition to mandatory standards indicators have been developed to assess the removal performance of WWTPs. In Austria, for example, the performance indicator “LW” (German: “Leistungskennwert”) has been designed to enable the comparison of the removal performance of different WWTPs using a single indicator. The LW sums up the concentrations of COD, total phosphorus,  $\text{NH}_4^+$  and  $\text{NO}_3^-$  and

additionally assigns them with different weighting factors to better represent the different environmental harming potential (Spatzierer, et al., 2000). Another indicator, the Effluent Quality Index (EQ) is used in one of the most important software for simulation of WWT, the Benchmarking Simulation Model (BSM). It considers the load of COD, BOD<sub>5</sub>, SS, NO<sub>3</sub><sup>-</sup> and TKN in the effluent within a defined time period (Vanrolleghem & Gillot, 2002), (Nopens, et al., 2010). To date, however, emissions of the greenhouse gas N<sub>2</sub>O from nitrification and denitrification processes do not play a role in the assessment of the WWTP's performance. The only evaluation method that allows consideration of N<sub>2</sub>O emissions and therefore, can provide a more comprehensive evaluation of WWT facilities, is Life Cycle Assessment (LCA) (Roeleveld, et al., 1997), (Tilman A.M., 1998), (Lundin, et al., 2000), (Tarantini & Ferri, 2001), (Doka & Hirschier, 2004), (Foley, et al., 2007), (Hospido, et al., 2007), (Renou, et al., 2008), (Vince, et al., 2008), (Lim & Park, 2009). Within LCA the nitrogen compounds are considered in their potential to cause eutrophication, acidification, global warming, eco-, and human toxicity. However, the LCA studies can be incomparable to each other due to the choice of the functional unit, the spatial and temporal boundaries of the particular study, and the impact weighting, for instance.

The term entropy was first defined by Clausius in the context of his formulation of the second law of thermodynamics (Clausius, 1865). However, the phenomena associated with entropy were described already before by the concept of heat (Black, 1803), (Carnot, 1824). In thermodynamics, entropy describes the loss of useful energy (exergy) due to irreversible processes such as the melting of an ice cube, friction or the free expansion of a gas (Tipler, 1994), (Schlichting, 2000), (Atkins & de Paula, 2001). The stochastic nature of thermodynamic processes was described based on the evolution of the theory of gases and statistical entropy was introduced as a measure of the possible microscopic compositions (e.g. location of gas molecules and their occupation of the translational, rotational and vibrational energy states) for a given macrostate (e.g. the temperature and pressure of the gas in a reservoir) (Boltzman, 1923). In his considerations, Boltzmann assumed an isolated system where all microstates are equally probable (microcanonical ensemble) and defined his formula for single particle distribution ignoring both the internal energy and the effect of interparticle forces on the pressure. Hence, the Boltzmann-entropy equals the thermodynamic entropy only for a perfect gas. Gibbs then extended the definition of statistical entropy considering a system consisting of an arbitrarily amount of particles that exchange energy with a reservoir. Gibbs' entropy formula is valid for all probability

distributions and if maximized, Gibbs entropy numerically results in the thermodynamic entropy. Consequently, Boltzmann's formula can be derived from the Gibbs formula (Jaynes, 1965). Gradually, entropy was also generalized to quantum mechanics, leading to a more general definition for entropy that is valid for every ensemble and from which the more specific formulas such as Boltzmann's and Gibbs' one can be derived (von Neumann, 1932), (Santillán, et al., 2008).

The connection between statistical entropy and information was comprehensively described by Shannon who showed that entropy can be regarded as a measure of the average information content (Shannon, 1948). At about the same time, information was also linked to energy in search of a solution to Maxwell's demon (Szilard, 1929), (Brillouin, 1950), (Brillouin, 1951), (Brillouin, 1951), (Landauer, 1961). Maxwell's idea about an experimental setup that would reverse a spontaneous thermodynamic reaction to produce work after each cycle would principally mean a violation of the 2<sup>nd</sup> law of thermodynamics. This problem was solved by integrating the concept of storage and erasure of information to this setup. The erasure of information generates entropy, a fact known as the Landauer-principle (Landauer, 1961). Considering information, Maxwell's experiment would thus comply with the second law of thermodynamics because the total entropy would still increase. In the meantime it has been shown that information erasure is possible without an energy cost, an increase in total entropy however is inevitable (Vaccaro & Barnett, 2011).

Statistical entropy has ever since been exploited as a measure of the dispersion of probability distributions. This implicates the manifoldness of applications of statistical entropy to all sorts of fields ranging from sociology, over economy, insurance to biogeographics, texture analysis, power systems, geophysical sciences, and water engineering (Georgescu-Roegen, 1987), (Marwan & Kurths, 2002), (Roulston & Smith, 2002), (Wöhlcke, 2003), (Böhlke, 2005), (Li, et al., 2005), (Maruyama, et al., 2005), (Phillips, et al., 2006), (Pires & Perdigao, 2007), (Bagchi, 2009), (Mogheir, et al., 2009), (Niemes & Schirmer, 2010), (Sakalauskas & Kriksciuniene, 2011), (Singh, 2013). In this context, the metric entropy has been widely interpreted in terms of randomness or disorder, unbiasedness or objectivity, equality, diversity, lack of concentration, flexibility, complexity, departure from uniform distribution, redundancy, or organization. Eventually all these interpretations use entropy as measure of the information content or missing (dissipated) information. The huge number of applications of entropy demonstrates its vast potential. Especially relevant for this work is the use of statistical

entropy to quantify dissipative losses from anthropogenic cycles. Tai and Goda demonstrated already in the 1980ies the benefit of using entropy to quantify the pollution of water and the thermodynamic efficiency of water treatment systems such as reverse osmosis (Tai & Goda, 1980), (Goda, et al., 1981), (Tai & Goda, 1985). However, water pollution was continuously described by concentrations of several chemical species while independently ways were found to decrease the energy demand of wastewater treatment facilities. Almost twenty years later, Larsen and Gujer reanimated the use of entropy in environmental science recommending the consideration of the second law of thermodynamics for a successful resource management. They highlighted the irreversibility of dilution (dissipation) of nutrients in the environment, argued that an efficient use of resources will lead to a minimal increase in entropy, and identified how this could lead to a more sustainable concept of wastewater design (Larsen & Gujer, 1997). A few years later, Rechberger applied statistical entropy to evaluate the power of a process to concentrate respective dilute chemical elements (Rechberger, 1999), (Rechberger & Brunner, 2002). Statistical Entropy Analysis (SEA) was primarily used to assess the efficiency of waste incinerators with respect to their dilution of heavy metals in the environment (Rechberger, 1999), (Rechberger, 2001), (Rechberger, 2012). Furthermore, SEA was utilized for the evaluation of the European copper cycle. In this work it was found that SEA can be applied to complex processes containing numerous flows and that today's successful copper management is a cycle of dilution and concentration of copper (Rechberger & Graedel, 2002). Following the evaluation of the European copper cycle, SEA was also used to assess the Chinese copper cycle (Yue, et al., 2009). In another study, SEA was exploited for the evaluation of the global warming potential of waste management systems (Kaufmann, et al., 2008). Yet, so far, SEA is only applicable to chemical elements while the chemical specification of an element such as nitrogen is often of particular importance.

The aim of this dissertation therefore is to extend SEA to chemical compounds and to test the reliability and usefulness of the extended SEA (eSEA) for the evaluation of two different systems that are relevant to water resources: farming regions and WWTPs. For this purpose, eSEA is first developed in Chapter 2 and then demonstrated on the basis of the nitrogen budget of a hypothetical region consisting of crop farming. Based on different emission scenarios the shortcomings of SEA are demonstrated and it is highlighted how these can be overcome by using eSEA. In Chapter 3, eSEA is applied to the nitrogen budgets of real agricultural production systems and that way, the

nitrogen performance of two Austrian catchments and of entire Austria is assessed. The findings are compared to the different nitrogen-use-efficiencies (NUEs) and the advantages and disadvantages of eSEA compared to the NUE are discussed. Chapter 4 examines the potential of eSEA for the assessment of the nitrogen removal performance of WWTPs. Therefore, it is applied to numerous Austrian WWTPs. The eSEA results are also set in relation to economic parameters such as the energy consumption and costs. In Chapter 5, eSEA is implemented into the effluent quality index of the WWT simulating software, the Benchmarking Simulation Model N°2 (BSM N°2) and the newly defined indicator is discussed in terms of suitability for evaluation of the WWT cleaning performance. Chapter 6 ultimately summarizes the main findings and implications of this work.

## Author`s contribution to the doctoral thesis

**Chapter 2** of this doctoral thesis is based on the publication “Extension of statistical entropy analysis to chemical compounds” by Sobańtka A., Zessner M. and Rechberger H. (2012), *Entropy*, 14, 2413-2426. The contribution of Alicja Sobańtka to this paper was:

- Development of extended Statistical Entropy Analysis (eSEA) including all mathematical equations
- Construction of emission scenarios of a hypothetical crop farming region
- Application of both SEA and eSEA to the presented variations of the hypothetical crop farming region, the discussion and the interpretation of the results

**Chapter 3** of this doctoral thesis is based on the publication “Extended Statistical Entropy Analysis for the evaluation of regional nitrogen budgets in Austria” by Sobańtka A., Thaler S., Zessner M. and Rechberger H., submitted to the *International Journal of Environmental Science and Technology*. The contribution of Alicja Sobańtka to this paper was:

- Preparation of the data
- Application of eSEA to the introduced systems and the interpretation of the results
- Construction of emission scenarios, application of eSEA to these scenarios, the discussion and interpretation of the results
- Sensitivity analysis

**Chapter 4** of this doctoral thesis is based on the publication “Extended Statistical Entropy Analysis (eSEA) for improving the evaluation of Austrian wastewater treatment plants” by Sobańtka A. and Rechberger H. (2013), *Water Science & Technology*, 67.5, 1051-1057. The contribution of Alicja Sobańtka to this paper was:

- Application of eSEA for the assessment of the nitrogen removal performance of WWTPs
- Comparison of the eSEA results to the individual nitrogen removal rates, the discussion and interpretation of these results

- Relation of the eSEA results to the energy consumption and the costs associated with the mechanical - biological treatment
- Comparison and discussion of the energy-efficiency and cost-effectiveness of small and large WWTPs

**Chapter 5** of this doctoral thesis is based on the publication “Implementation of Extended Statistical Entropy Analysis to the Effluent Quality Index of the Benchmarking Simulation Model N°2” by Sobańtka A., Pons M.-N., Zessner M. and Rechberger H., submitted to the *Water* Journal. The contribution of Alicja Sobańtka to this paper was:

- Performance of the different BSM N°2 simulations
- Application of eSEA to assess the nitrogen removal performance of the different simulations
- Implementation of eSEA to the EQ and the definition of  $\Delta EQ_{new}$
- Comparison and discussion of the traditional EQ and  $\Delta EQ_{new}$
- Scenario analysis generating different, realistically expectable N<sub>2</sub>O emissions, the assessment according to  $\Delta EQ_{new}$  and the discussion of these results

## 2 The Extension of Statistical Entropy Analysis to Chemical Compounds

### Abstract

Statistical entropy analysis (SEA) quantifies the dilution and concentration of conservative substances (e.g., heavy metals) in a system. In this chapter, the SEA concept is extended (eSEA) to make it applicable to systems in which the chemical speciation is of particular importance. The eSEA is applied to a simplified region used for crop farming. The extent to which the region concentrates or dilutes nitrogen compounds is expressed as the change in statistical entropy ( $\Delta H$ ). A detailed derivation for the calculation of  $\Delta H$  is provided. The results are discussed for four variations of the crop farming system, showing that the efficiency of crop farming can be expressed by eSEA.

### 2.1 Introduction

Developed in the 1980s, material flow analysis (MFA) is a technique that tracks the flows of goods and substances between processes and through a defined system (Baccini & Brunner, 1991). Processes that transform input goods into different output goods concentrate and dilute various substances. Concentration usually occurs when products and byproducts are manufactured from raw materials, wastes are collected or materials are recovered from waste. Dilution occurs when materials are mixed (as in the fabrication of complex products) or emissions are released to the environment. With regard to material management, concentration is generally considered as a positive and beneficial process because it increases the availability of a material. Dilution, however, is easier to accomplish than concentration, although it represents a disadvantage due to increased expenses for material recovery. On the other hand, a certain degree of dilution is acceptable as long as it complies with environmental protection regulations. Such concentration and dilution phenomena can be quantified by Statistical Entropy Analysis (SEA) (Rechberger & Brunner, 2002), (Rechberger & Graedel, 2002). SEA is based on Shannon's definition for statistical entropy in information technology (Shannon, 1948). The probability of an event is transformed into the probability of appearance of a chemical element, expressed by its concentration. Therewith, statistical entropy becomes a tool used to quantify the distribution of conservative substances (e.g., particular chemical elements such as heavy metals) and



it is a tailor-made evaluation tool for MFA studies (in the following, we use MFA terminology; term definitions can be found in (Brunner & Rechberger, 2004)).

SEA can be illustrated through a simple cadmium budget of a process with two input flows that are transformed into two output flows (see Figure 2.1). Each flow is described by a mass flow rate ( $\dot{M}$ ) and the respective concentration of cadmium ( $c$ ). In a first step we assume  $\dot{M} = 1$  and replace the probabilities in Shannon's entropy formula [Equations (1) and (2)] by concentrations [Equations (3) and (4)]. If the concentration in a flow is 100%, then the probability to find cadmium in it is 100%. Equation 3 is applied to the input ( $H_{IN}$ ) and the output ( $H_{OUT}$ ) of the process and the change is expressed as  $\Delta H = H_{OUT} - H_{IN}$  (in Thermodynamics the letter "H" is used for enthalpy while "S" designates entropy. However, we use "H" to make clear that entropy as applied here is derived from statistical entropy where "H" is used):

$$H = -\sum_{i=1}^k P_i * \log_2(P_i) \quad \text{Eq.2.1}$$

$$\sum_{i=1}^k P_i = 1 \quad \text{Eq.2.2}$$

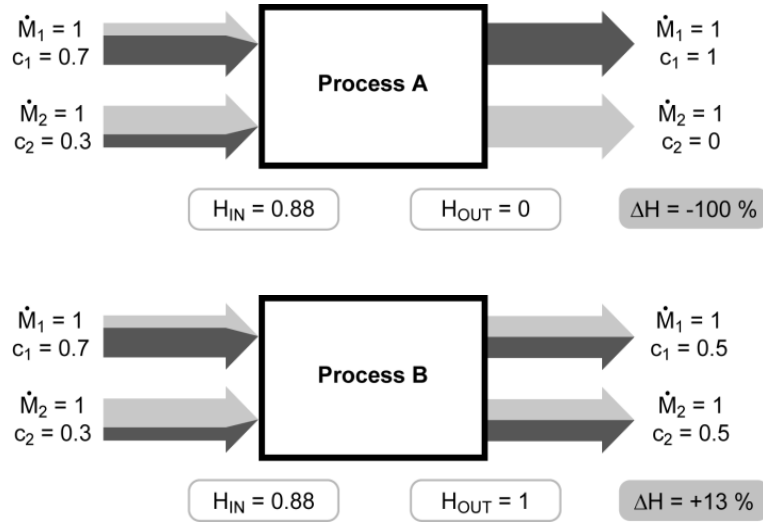
$$H(c_i) = -\sum_{i=1}^k c_i * \log_2(c_i) \quad \text{Eq.2.3}$$

$$\sum_{i=1}^k c_i = 1 \quad \text{Eq.2.4}$$

According to Shannon the maximum entropy is given for the equiprobability of all possible configurations:

$$H_{\max} = \log_2(k) \quad \text{Eq.2.5}$$

Transferred to the simple example in Figure 2.1, maximum entropy occurs if cadmium is equally distributed among the output flows (cf. Figure 2.1, Process B).



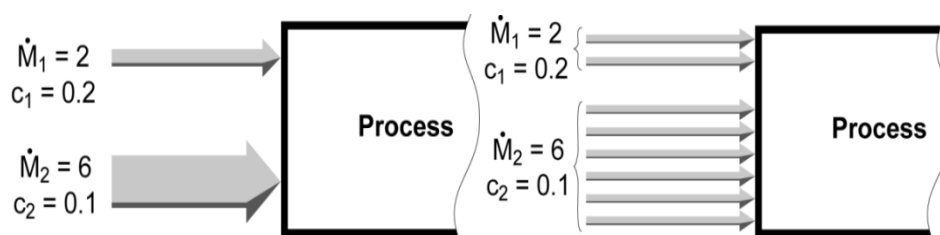
**Figure 2.1:** Simple cadmium budget of a process with two input flows that are transformed into two output flows. All mass flow rates  $\dot{M} = 1$ , the colors indicate the concentrations of cadmium. Process A achieves maximum concentrating of cadmium ( $H_{OUT} = 0$ ). Process B realizes the equal distribution of cadmium to both flows and  $H_{OUT} = H_{max} = 1$ .

However, for real processes  $\dot{M} \neq 1$  and the mass flow rates of the flows have to be considered, as it makes a difference if it is high or low. To consider  $\dot{M}$  the mass flow rate is interpreted as a frequency of occurrence: From a materials point of view a flow with  $\dot{M} = 6$  is the same as 6 flows with  $\dot{M} = 1$  (cf. Figure 2.2). The basic statistical entropy formula for the distribution of a substance in different material flows is then:

$$H(\dot{M}_i, c_i) = - \sum_{i=1}^k \dot{M}_i * c_i * \log_2(c_i) \quad \text{Eq.2.6}$$

$$\sum_{i=1}^k \dot{M}_i * c_i = 1 \quad \text{Eq.2.7}$$

$$H_{max} = \log_2 \left( \sum_{i=1}^k \dot{M}_i \right) \quad \text{Eq.2.8}$$



**Figure 2.2:** The real mass flow rates are interpreted as the frequency of occurrence of flows with  $\dot{M} = 1$ .

SEA has been applied to the European copper cycle, demonstrating that SEA can be applied to systems consisting of several processes, that a real system is a succession of concentration and dilution processes, and finally, that SEA is a powerful indicator for quantifying the quality of material management of processes and systems (Rechberger & Graedel, 2002). Further applications of SEA are reported in (Kaufmann, et al., 2008) and (Yue, et al., 2009).

Classical MFA addresses chemical elements (e.g., heavy metals or nutrients such as nitrogen or phosphorous). However, the chemical speciation of an element is often important to model. For instance, a simple nitrogen balance of a Waste-to-Energy (WtE) plant is of limited value because it is important to know whether the N leaves the plant as molecular nitrogen ( $N_2$ ), NO,  $NO_2$ ,  $NH_3$ ,  $NO_3^-$  or some other form. Therefore, in this paper, we want to extend the “classical” SEA to make it applicable to chemical compounds. To demonstrate how the extended Statistical Entropy Analysis (eSEA) is calculated and how the results can be used, we apply the method to a simplified hypothetical system consisting of a crop farming region that transforms nitrogen compounds. The aim of this chapter is to introduce the extended SEA and demonstrate its application to a simple system. The focus is not on an actual crop farming region.

## 2.2 Description of the Investigated System and Data

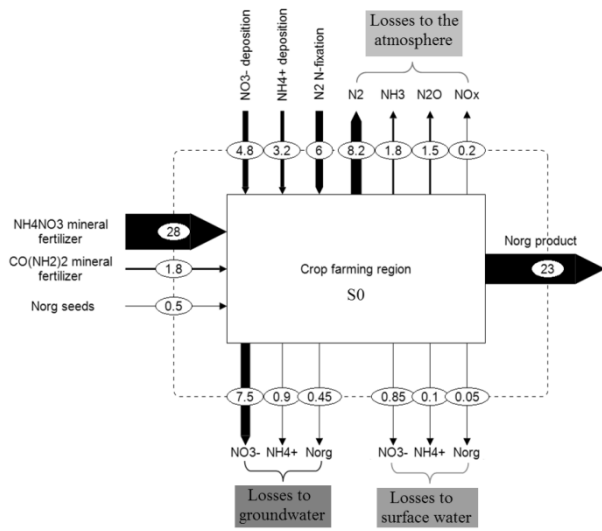
The investigated system is simple and consists of one process (crop farming), four input material flows (mineral fertilizer, seeds, deposition, and nitrogen fixation), and four output material flows (plant-based agricultural product, losses to the atmosphere, groundwater, and surface water) transforming various nitrogen compounds (e.g.,  $CO(NH_2)_2$ ,  $NO_3^-$ ,  $NH_4$ ,  $N_2$ ,  $NO_x$ , and  $N_2O$ ), as shown in Figure 2.3a (base system S0). The system represents a hypothetical region where crop farming is practiced. This farming region yields a product (plant-derived protein expressed as  $N_{org}$ ). Different

processes are used to describe the nitrogen transformation and transport. Deposition in the form of rain and snow usually brings  $\text{NO}_3^-$  and  $\text{NH}_4^+$  into the region.  $\text{N}_2$  is adsorbed and then oxidized by microorganisms, resulting in higher nitrogen availability in the soil (nitrogen fixation). Emissions to ground and surface water typically occur as  $\text{NO}_3^-$ ,  $\text{NH}_4^+$ , and  $\text{N}_{\text{org}}$ . Mineral fertilizer is assumed to be a mixture of urea  $[\text{CO}(\text{NH}_2)_2]$  and ammonium nitrate ( $\text{NH}_4\text{NO}_3$ ), and seeds contain  $\text{N}_{\text{org}}$  in the form of protein. Gaseous losses are mostly  $\text{NH}_3$ ,  $\text{N}_2$  and, to a lesser extent,  $\text{N}_2\text{O}$  and other oxides of nitrogen ( $\text{NO}_x$ ) (see Figure 2.3).

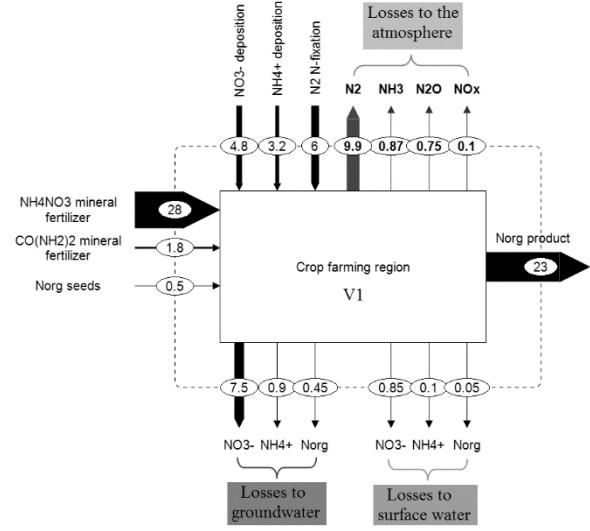
Data are taken from a study on nutrient balances for Austria and Hungary (Zessner, et al., 2004). All data correspond to an area of 1 hectare and a time scale of 1 year. In this way, regions of different dimensions can be compared to each other.

In this chapter, three explicit system variations are selected to demonstrate how the eSEA works. Practical implications of these emissions scenarios are not the focus of this work. In variations V1 and V2, the gaseous emissions are modified. In variation V3, the emissions to surface and groundwater are changed. However, the system's total nitrogen throughput always remains the same. Figure 2.3b presents variation V1. In this variation, the gaseous emissions of  $\text{NH}_3$ ,  $\text{N}_2\text{O}$  and  $\text{NO}_x$  are each reduced by 50% relative to the original system S0 for the benefit of  $\text{N}_2$  (cf. Figure 2.3a). In the second variation (V2), the gaseous emissions of  $\text{NH}_3$ ,  $\text{N}_2\text{O}$  and  $\text{NO}_x$  are each increased by 50% relative to the base system S0, and the emission of  $\text{N}_2$  is reduced accordingly (cf. Figure 2.3c). Finally, a variation is created (V3) in which the emissions to surface and groundwater are decreased by 50% for the benefit of the product (cf. Figure 2.3d). To classify the eSEA results, both an optimal and a worst case scenario are introduced as well. Both scenarios are highly fictitious, but they serve as a reference. Optimal nitrogen management in our exemplary region would mean that all nitrogen is transferred into the farming product (cf. Figure 2.3e). In this case, the eSEA yields the best result, which is minimal entropy production or, in other words, minimal dilution. In the theoretical worst case scenario, the nitrogen that comes into the region is transformed to organic nitrogen and emitted to groundwater (Figure 2.3f). This scenario yields the worst result, which is equivalent to maximum entropy generation or maximum dilution. High entropy generation occurs if a nitrogen compound is emitted into an environmental compartment with a low natural background concentration of that particular nitrogen compound (see Section 3.3).

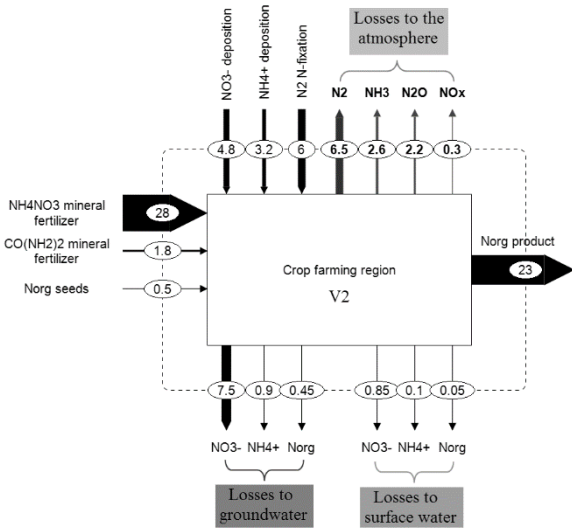
## 2. The Extension of Statistical Entropy Analysis to Chemical Compounds



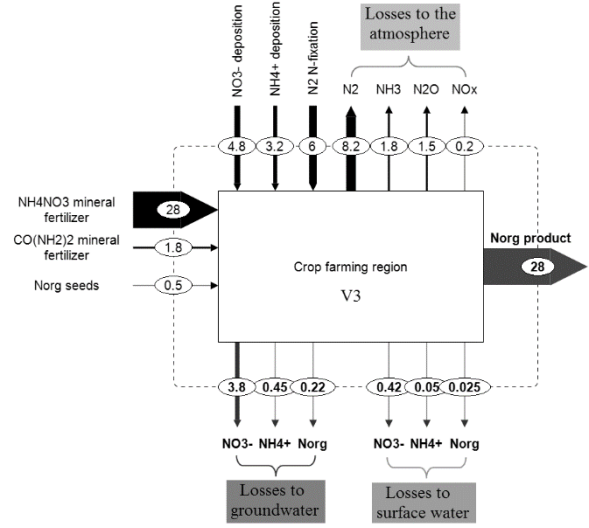
(a) Base system S0



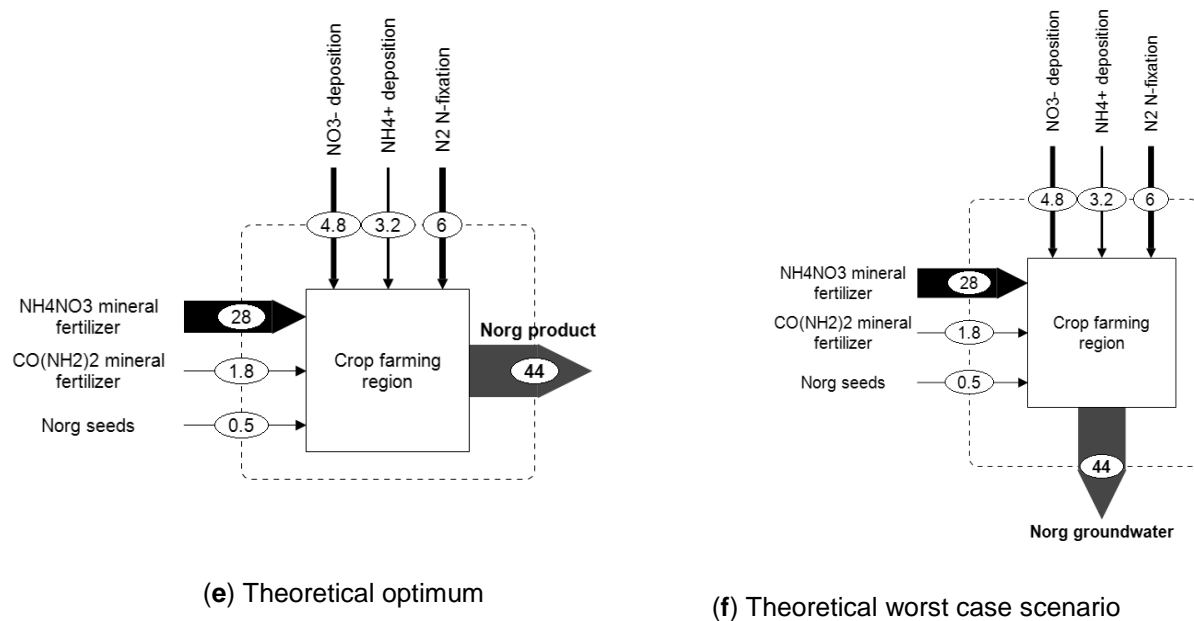
(b) Variation V1: emissions of  $\text{NH}_3$ ,  $\text{N}_2\text{O}$ , and  $\text{NO}_x$  are each reduced by 50% (green)



(c) Variation V2:  $\text{NH}_3$ ,  $\text{N}_2\text{O}$  and  $\text{NO}_x$  are each increased by 50% (red)



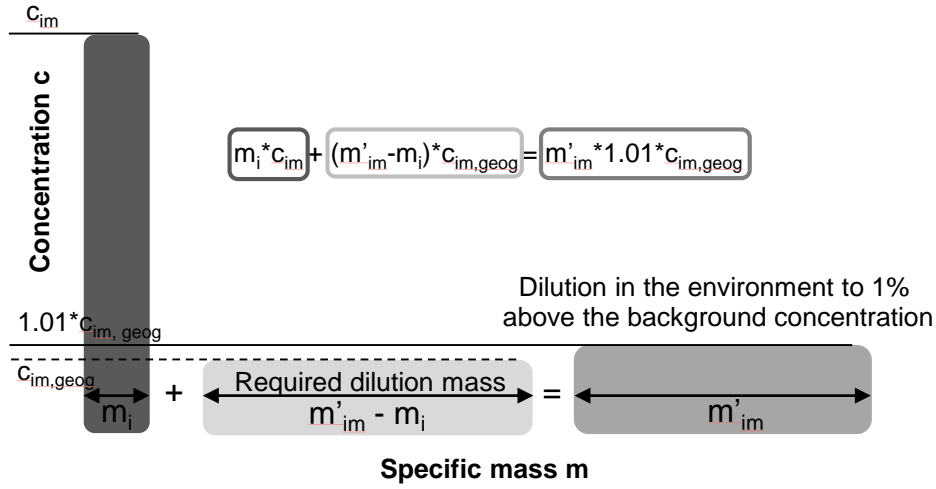
(d) Variation V3: emissions to surface and groundwater are each decreased by 50% (green)



**Figure 2.3:** Nitrogen budgets for a hypothetical and simplified crop farming region based on Austrian data (data rounded); all values are given in kgN/ha/yr.

## 2.3 Extension of the Statistical Entropy Analysis (eSEA)

For a comprehensive derivation of the SEA (formulas and assumptions), see Rechberger and colleagues (Rechberger, 1999), (Rechberger & Brunner, 2002), (Rechberger & Graedel, 2002). The extension of the SEA to chemical compounds (eSEA) is based on the equations given in (Rechberger & Brunner, 2002) and (Rechberger, 1999) and is explained on the basis of the hypothetical crop farming system presented above (cf. Figure 2.3). Therefore, the most important principles of the SEA are addressed in this paper and the main equations are contrasted with the equations of the extended SEA (see Table 2-1).



**Figure 2.4:** Illustration of the dilution process of an emission.

The mass balance principle requires that the total amount of incoming nitrogen equals the total amount of nitrogen that is leaving the system, assuming that there is no storage of nitrogen compounds in the region (i.e., steady-state conditions; storage phenomena are not considered here but could be considered as shown in (Rechberger & Graedel, 2002)). The mass flows (such as the amounts of rainwater, fertilizer, and product) indicated by  $\dot{M}_i$  (index  $i$  for flows), and the concentrations of the individual nitrogen compounds ( $c_{im}$ , index  $m$  for compounds) are the required basic data. Concentrations of nitrogen compounds are used as concentrations of pure nitrogen in a particular mass flow. A description of all indices and parameters (including their physical units) is given at the end of this thesis. Before the statistical entropy can be calculated, some simple normalization steps are required to convert these data ( $\dot{M}_i$ ,  $c_{im}$ ) into corresponding dimensionless values. This allows for a comparison of systems of different sizes. First, the nitrogen loads ( $\dot{X}_{im}$ ) for all nitrogen compounds in a particular material flow in the input and output are computed according to Equation 2.9:

$$\dot{X}_{im} = \dot{M}_i * c_{im} \quad \text{Eq. 2.9}$$

$$m_i = \frac{\dot{M}_i}{\sum_{i=1}^k \sum_{m=1}^r \dot{X}_{im}} \quad \text{Eq. 2.10}$$

where  $k$  is the number of input material flows (here,  $k = 4$ : fertilizer, seeds, deposition, nitrogen fixation), and  $r$  is the number of different nitrogen compounds that appear in the input flows [here,  $r=6$ :  $\text{NH}_4^+$ ,  $\text{NO}_3^-$ ,  $\text{CO}(\text{NH}_2)_2$ ,  $\text{NH}_4\text{NO}_3$ ,  $\text{N}_{\text{org}}$ ,  $\text{N}_2$ ].

The denominator of Equation 2.10 is the total flow of nitrogen through the system, so the specific masses  $m_i$  are related to one mass-unit of nitrogen (e.g., kg fertilizer input per kg total nitrogen throughput).

Next, the specific loads  $X_{\text{im}}$  that describe the fractions of each nitrogen compound with respect to the total nitrogen in the different material flows are calculated as:

$$X_{\text{im}} = m_i * c_{\text{im}} \quad \text{Eq. 2.11}$$

The sum of all specific nitrogen loads for each nitrogen compound must be 100% for both the input and output (mass balance principle). In mathematical terms, we have:

$$\sum_{i=1}^k \sum_{m=1}^r X_{\text{im}}^{\text{IN}} = 1 \quad \text{Eq. 2.12}$$

$$\sum_{i=1}^l \sum_{m=1}^s X_{\text{im}}^{\text{OUT}} = 1 \quad \text{Eq. 2.13}$$

where  $l$  is the number of all outgoing material flows (here,  $l = 4$ : product and losses to the atmosphere, groundwater, and surface water), and  $s$  represents the number of nitrogen compounds in the output (here,  $s=7$ :  $\text{NO}_3^-$ ,  $\text{NH}_4^+$ ,  $\text{N}_{\text{org}}$ ,  $\text{NH}_3$ ,  $\text{NO}_x$ ,  $\text{N}_2\text{O}$ ,  $\text{N}_2$ ). The definitions of  $k$  and  $r$  are as given above.

### 2.3.1 Estimation of the Statistical Entropy of the Input ( $H_{\text{IN}}$ )

The extended statistical entropy is first calculated for the nitrogen input into the system. In reference to the system presented in this work, statistical entropy of the input is the sum of the statistical entropy values for  $\text{CO}(\text{NH}_2)_2$  and  $\text{NH}_4\text{NO}_3$  in the mineral fertilizer,  $\text{N}_{\text{org}}$  in the seeds,  $\text{NH}_4^+$  and  $\text{NO}_3^-$  from deposition, and  $\text{N}_2$  from N-fixation. The equivalent for the SEA would be the sum of the statistical entropy values for the total nitrogen from the mineral fertilizer, seeds, deposition, and nitrogen fixation with no differentiation among nitrogen species (see Table 2-1).



**Table 2-1:** Calculation of the statistical entropy for the input; left side: classical SEA; right side: extended SEA.

SEA	eSEA
$H_{IN,N}(m_i, c_{iN}) = - \sum_{i=1}^k m_i * c_{iN} * \log_2(c_{iN})$ <p>(Eq.2.1)</p> <p>Entropy is a function of the <b>total nitrogen load (N)</b> in the different input flows</p>	$H_{IN}(m_i, c_{im}) = - \sum_{i=1}^k \sum_{m=1}^r m_i * c_{im} * \log_2(c_{im})$ <p>(Eq.2.2)</p> <p>Entropy is a function of the load of all <b>nitrogen compounds (m)</b> that appear in the different input flows</p>

### 2.3.2 Estimation of the Statistical Entropy of the Output ( $H_{OUT}$ )

Nitrogen that is not transferred to a solid product is either diluted in the atmosphere (gaseous losses) or in the hydrosphere (surface and groundwater) in the form of different nitrogen compounds. Dilution leads to an entropy increase. This is considered in the calculations by the assumption that the emissions are diluted up to a concentration that is 1% above the corresponding background concentration ( $c_{im,geog}$ ) in the receiving environmental compartment (cf. Figure 2.4; see Equations 2.18–2.21 in Table 2-2). It has been shown that this assumption represents the real dilution process with sufficient accuracy (Rechberger, 1999).

**Table 2-2:** Calculation of the statistical entropy for the output; left side: classical SEA; right side: extended SEA.

SEA	eSEA
$H_{\text{OUT},N} = (m'_i, c'_{iN}) = - \sum_{i=1}^l m'_i * c'_{iN} * \log_2(c'_{iN})$ <p>(Eq.2.16)</p> <p>Entropy for the output depends on <b>total nitrogen loads (N)</b> in the different output flows</p>	$H_{\text{OUT}}(m'_{im}, c'_{im}) = - \sum_{i=1}^l \sum_{m=1}^s m'_{im} * c'_{im} * \log_2(c'_{im})$ <p>(Eq.2.17)</p> <p>Entropy depends on the load of all <b>nitrogen compounds (m)</b> that appear in the different output flows</p>
<b>CALCULATION OF THE DILUTING TERMS</b>	
$m'_i = m_i * \frac{c_{iN} - c_{iN,geog}}{c_{iN,geog}} * 100 + m_i$ <p>(Eq.2.18)</p>	$m'_{im} = m_i * \frac{c_{im} - c_{im,geog}}{c_{im,geog}} * 100 + m_i$ <p>(Eq.2.19)</p>
$c'_{iN} = \frac{c_{iN} * c_{iN,geog}}{c_{iN} - 0.99 * c_{iN,geog}} * 0.01$ <p>(Eq.2.20)</p>	$c'_{im} = \frac{c_{im} * c_{im,geog}}{c_{im} - 0.99 * c_{im,geog}} * 0.01$ <p>(Eq.2.21)</p>

To calculate the statistical entropy for gaseous (NH<sub>3</sub>, N<sub>2</sub>, NO<sub>x</sub>, N<sub>2</sub>O) and aqueous emissions (NH<sub>4</sub><sup>+</sup>, NO<sub>3</sub><sup>-</sup>, N<sub>org</sub>), the specific masses  $m_i$  from Equation 2.10 are replaced by so-called diluting masses (see Equation 2.19 in Table 2-2). The corresponding specific concentrations are given by Equation 2.21. The atmospheric background concentrations used in this paper are taken as the mean values from the ESPERE Climate Encyclopedia (Uherek, 2004). Both the NO<sub>3</sub><sup>-</sup> and NH<sub>4</sub><sup>+</sup> background concentrations in surface and groundwater are set in accordance with a very good ecological status of water bodies according to the Austrian Water Act (BGBl II Nr, 98/2010), (BGBl II Nr, 99/2010), (BGBl II Nr, 461/2010). Organically bound nitrogen is rarely present in the hydrosphere, so its background concentration is assumed to be approximately four orders of magnitude smaller than the background concentration for NH<sub>4</sub><sup>+</sup>. In principle, other reference concentrations could be used to perform the eSEA, such as eco-toxicological safety values. In this case, the result could be interpreted as eco-toxicological harming potential. Such an approach has not yet been systematically

investigated. For nitrogen in the product, no further dilution is considered because consumption and use are not part of the investigated system.

### 2.3.3 Estimation of the Maximum Statistical Entropy of the Output ( $H_{\max}$ )

To rank the results, a maximum entropy ( $H_{\max}$ ) is defined according to the theoretical worst case scenario (cf. Figure 2.3f when all N is transferred into the groundwater). The statistical entropy values ( $H_{\text{IN}}$ ,  $H_{\text{OUT}}$ ) are then divided by  $H_{\max}$  to obtain normalized values between 0 and 1.

**Table 2-3:** Calculation of the maximum statistical entropy  $H_{\text{MAX}}$ .

<b>SEA</b>
$H_{\max} = \log_2 (m'_{i,\max}) = \log_2 \left( \frac{1}{\min(c_{N,\text{geog}})} * 100 \right)$ <p>(Eq.2.22)</p> <p>With <math>\min(c_{N,\text{geog}})=1\text{E-}05 \text{ kgN/kg }^{(1)}</math></p>
<b>eSEA</b>
$H_{\max} = \log_2 (m'_{\text{im},\max}) = \log_2 \left( \frac{1}{\min(c_{m,\text{geog}})} * 100 \right)$ <p>(Eq.2.23)</p> <p>With <math>\min(c_{m,\text{geog}})=7\text{E-}11 \text{ kgN/kg }^{(2)}</math></p>

<sup>(1)</sup> Approximates the total nitrogen concentration in groundwater

<sup>(2)</sup> Approximates the nitrogen concentration of  $N_{\text{org}}$  in groundwater

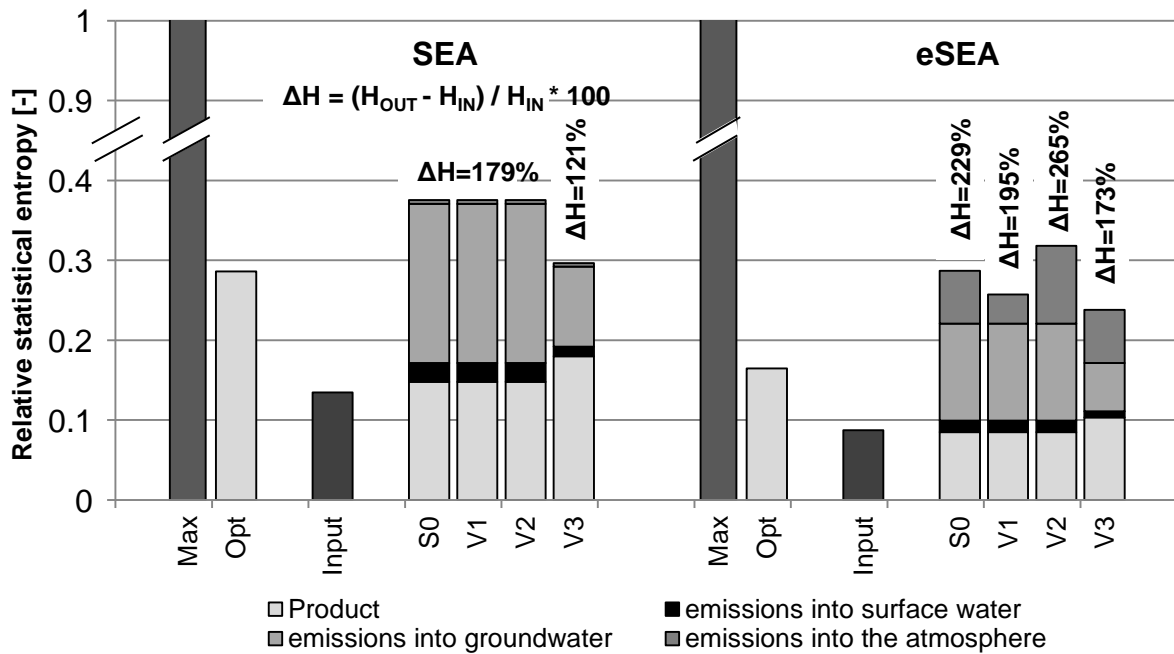
### 2.3.4 Estimation of the Concentrating Power/Diluting Extent, $\Delta H$

If the output entropy is lower than the input entropy, concentration takes place. With regard to the crop farming region, this means that nitrogen in its various chemical compositions is concentrated through different processes. If the output entropy equals the input entropy, the nitrogen is neither diluted nor concentrated. The region dilutes nitrogen if the output entropy is higher than the input entropy. This dilution / concentration can be expressed as a % difference in statistical entropy,  $\Delta H$ :

$$\Delta H = \frac{H_{OUT} - H_{IN}}{H_{IN}} * 100 \quad (\text{Eq.2.14})$$

### 2.3.5 SEA vs. eSEA

In a next step the requirement for the extension of the SEA to chemical compounds is demonstrated by a comparison between SEA and eSEA. Both SEA and eSEA are applied to the presented crop farming system, and different evaluation results are obtained from the eSEA compared to the SEA (cf. Figure 2.5 and Table 2-4).



**Figure 2.5:** Relative statistical entropy values for the input and output of the base system (S0) and all variations (V1–V3) according to SEA and eSEA for the hypothetical crop farming region; entropy values are divided into entropy contributions from product yield and losses to the atmosphere, surface water, and groundwater.

Both the SEA and eSEA confirm that nitrogen is diluted through the crop farming region ( $\Delta H > 0$ ). This is the case because the nitrogen in the fertilizer is more concentrated than that in the product: a typical result for a system where products are consumed or used. For both methods, the dilution lies in the range between the theoretical optimum and the theoretical worst case scenario ( $H_{rel} = 1$ ). Note that the entropy results for the theoretical optimum are different for the SEA ( $H_{opt,rel} = 0.25$ ) and eSEA ( $H_{opt,rel} = 0.16$ ). This is due to the different input entropy values because, in contrast to the eSEA, the

individual nitrogen compounds are not differentiated in SEA. In general, the SEA shows more preferential results (lower  $\Delta H$ , less dilution) for systems S0–V3. However, neither a 50% reduction in gaseous emissions according to scenario V1 nor a 50% emission increase as described in scenario V2 are rewarded by the SEA because the total gaseous nitrogen emission does not change. Scenario V1 is clearly preferable due to its lower emissions of  $\text{NH}_3$ ,  $\text{N}_2\text{O}$  and  $\text{NO}_x$ . The eSEA accounts for this result by calculating a lower extent of dilution ( $\Delta H = 195\%$ ) in comparison to the original state ( $\Delta H = 229\%$ ). Variation V2 is assessed with a higher  $\Delta H$  of 265%. Lower  $\Delta H$  values are obtained from both SEA and eSEA if emissions into the hydrosphere (surface and groundwater) are each decreased by 50% (V3). The SEA achieves a significantly better result for V3 ( $\Delta H = 121\%$ ) than the eSEA ( $\Delta H = 173\%$ ) because the SEA calculates the entropy generation from the sum of nitrogen being released into surface and groundwater while referring to a single corresponding nitrogen background concentration. On the other hand, the eSEA quantifies the entropy contribution from each nitrogen compound that is emitted into the hydrosphere with respect to the different corresponding background concentrations.

## 2.4 Application of the eSEA: A Numerical Example

In this section, a calculation for the system S0 (cf. Figure 2.3a) is given. Table 2-4 shows all relevant data along with intermediate results. Table 2-5 displays the final results.

**Table 2-4:** Calculation of the maximum statistical entropy  $H_{\text{MAX}}$ .

				(Eq.2.9)	(Eq.2.10)	(Eq.2.11)	(Eqs.2.12, 2.13)
				$\dot{X}_{\text{im}}$	$m_i$	$X_{\text{im}}$	$\sum X_{\text{im}}$
				kgN/a	kg/kgN	kgN/kgN	kgN/kgN
INPUT	Fertilizer	211			4.74		1
	$\text{NH}_4\text{NO}_3$		0.13	28.20		0.63	
	$\text{CO}(\text{NH}_2)_2$		0.01	1.80		0.04	
	Seeds	25			0.56		
	$\text{N}_{\text{org}}$		0.02	0.50		0.01	

	<b>Deposition</b>	<b>571</b>				<b>12.84</b>		
	NO <sub>3</sub> <sup>-</sup>		0.01		4.80		0.11	
	NH <sub>4</sub> <sup>+</sup>		0.01		3.20		0.07	
	<b>N-fixation</b>	<b>8</b>	0.76		6.00	<b>0.18</b>	0.13	
<b>OUTPUT</b>	<b>Product</b>	<b>2300</b>				<b>51.68</b>		<b>1</b>
	N <sub>org</sub>		0.01		23.00		0.52	
	<b>Off-gas</b>	<b>11</b>				<b>0.24</b>		
	N <sub>2</sub>		0.7553	0.7553	8.19		0.18	
	NH <sub>3</sub>		0.16	4.1 E-9	1.75		0.04	
	N <sub>2</sub> O		0.14	2.0 E-8	1.50		0.03	
	NO <sub>x</sub>		0.02	2.5 E-10	0.20		4.5 E-03	
	<b>Surface water</b>	<b>42</b>				<b>0.94</b>		
	NO <sub>3</sub> <sup>-</sup>		2.0 E-02	3.0 E-06	0.85		0.02	
	NH <sub>4</sub> <sup>+</sup>		2.4 E-03	1.2 E-06	0.10		2.3 E-03	
	N <sub>org</sub>		1.2 E-03	1.0 E-10	0.05		1.1 E-03	
	<b>Groundwater</b>	<b>373</b>				<b>8.37</b>		
	NO <sub>3</sub> <sup>-</sup>		2.0 E-02	1.0 E-05	7.52		0.17	
	NH <sub>4</sub> <sup>+</sup>		2.4 E-03	3.5 E-07	0.90		0.02	
	N <sub>org</sub>		1.2 E-03	7.0 E-11	0.45		0.01	

**Table 2-5:** Final results for the eSEA on nitrogen compounds in the hypothetical crop farming region based on Austrian data (data rounded) and base system S0.

		(Eq.2.19)	(Eq.2.21)	(Eqs.2.15, 2.17)		(Eq.2.23)	(Eq.2.24)
		m'im	c'im	H <sub>IN</sub> / H <sub>OUT</sub>	H <sub>IN,rel</sub> / H <sub>OUT,rel</sub>	H <sub>max</sub>	ΔH
		[-]	[-]	[-]	[-]	[-]	[%]
INPUT	Fertilizer			3.52	0.09		
	NH <sub>4</sub> NO <sub>3</sub>						
	CO(NH <sub>2</sub> ) <sub>2</sub>						
	Seeds						
	N <sub>org</sub>						
	Deposition						
	NO <sub>3</sub> <sup>-</sup>						
	NH <sub>4</sub> <sup>+</sup>						
	N-fixation						
OUTPUT	Product			11.60	0.29	40.38	229
	N <sub>org</sub>						
	Off-gas						
	N <sub>2</sub>	2.4 E-01	7.553 E-01				
	NH <sub>3</sub>	9.6 E+08	4.1 E-11				
	N <sub>2</sub> O	1.7 E+08	2.0 E-10				
	NO <sub>x</sub>	1.8 E+08	2.0 E-12				
	Surface water						
	NO <sub>3</sub> <sup>-</sup>	6.4 E+05	3.0 E-08				
	NH <sub>4</sub> <sup>+</sup>	1.9 E+05	1.2 E-08				

	N <sub>org</sub>	1.1 E+09	1.0 E-12				
	<b>Groundwater</b>						
	NO <sub>3</sub> <sup>-</sup>	1.7 E+06	1.0 E-07				
	NH <sub>4</sub> <sup>+</sup>	5.8 E+06	3.5 E-09				
	N <sub>org</sub>	1.4 E+10	7.0 E-13				

## 2.5 Conclusions

This chapter presents an evaluation method based on statistical entropy (eSEA) for assessing the concentration and dilution of chemical compounds in a system. It demonstrates how eSEA can be applied to assess the nitrogen performance of a hypothetical crop farming region based on data from Austria. The results show that the optimal utilization of nitrogen (maximum yield) occurs with low entropy production and that significant losses of nitrogen to the environment produce entropy. Therefore, eSEA may have the potential to become a meaningful indicator for the quality of regional substance management. In the next chapter, we will apply eSEA to real (and more complex) Austrian regions to test its relevance for decision-making in regional nutrient management.



### **3 Extended Statistical Entropy Analysis for the evaluation of regional nitrogen budgets in Austria**

#### **Abstract**

In this chapter, extended statistical entropy analysis (eSEA) is used to evaluate the nitrogen budgets of two Austrian catchments, the Wulka and the Ybbs, and of entire Austria. The eSEA enables quantification of the extent of nitrogen dilution based on the consideration of all types of nitrogen compounds and of the distribution of these compounds in various material flows. The results from the eSEA are compared to the corresponding nitrogen use efficiencies (NUEs). Application of the eSEA reveals that nitrogen is diluted to a greater extent in the Ybbs catchment than in the Wulka catchment, primarily as a result of increased losses of nitrogen compounds to the atmosphere and in leachates to the groundwater. The NUE in the Wulka catchment, at 63%, is substantially higher than that in the Ybbs catchment, at 43%, and confirms an improved nitrogen performance of Wulka. Furthermore, it is shown that the adoption of a healthy, balanced diet, as defined by the German Nutrition Society, changes the total nitrogen budget of Austria in a way that significantly lowers the dilution of nitrogen. Decreased nitrogen losses to the atmosphere and to the groundwater are primarily responsible for this result. In fact, the national NUE of Austria increases from 48% to 53%, if the Austrian nitrogen budget is calculated assuming the adoption of a healthy balanced diet. However, unlike the eSEA, the NUE does not reflect any changes in the nitrogen compounds emitted to the atmosphere or discharged to the surface water- and groundwater. Furthermore, inclusion of the uncertainty of the input data makes the comparison of the results of the NUE statistically insignificant. This study demonstrates the effectiveness of eSEA for the evaluation of nitrogen budgets in agricultural regions and suggests that statistical entropy can serve as a reliable agri-environmental indicator to support decision regarding nutrient management.

#### **3.1 Introduction**

Human activities have significantly increased the amount of reactive nitrogen (all N-compounds except N<sub>2</sub>) in the global N-cycle, particularly in industrialized countries (Galloway, et al., 2004), (Smil, 1999), (Vitousek, et al., 1997). The amount of reactive nitrogen continues to increase on a global scale, primarily as a result of agricultural activities (Galloway, et al., 2004), (Gruber & Galloway, 2008), (Nielsen, 2006), (Sutton,

et al., 2011). In fact, agriculture has been identified as the major source of increased reactive nitrogen emissions to both the atmosphere and surface and groundwater (Bouwman, et al., 1997), (Mosier, et al., 1998), (Van Drecht, et al., 2003). Smil (1999) has found that crop production is the principle cause of the anthropogenic alteration of the nitrogen cycle (Smil, 1999). The gap between the creation of reactive nitrogen and the nitrogen that is needed for human nutrition represents the nitrogen surplus (Galloway, et al., 2003). The nitrogen surplus is absorbed by the environment. In particular, this surplus nitrogen accumulates in the atmosphere and hydrosphere, causing environmental problems ranging from eutrophication to global acidification and ultimately contributing to climate change (Camargo & Alonso, 2006), (Bouwman, et al., 2005), (Gruber & Galloway, 2008), (Tilman, 1999), (Vitousek, et al., 1997). In addition, the nitrogen cycle interacts with other major biogeochemical cycles and can have serious consequences, particularly for the carbon cycle (Gruber & Galloway, 2008), (Vitousek, et al., 1997). Efforts have been made to reduce reactive nitrogen emissions with the help of environmental policies and tools such as the nitrogen footprint calculator. These initiatives should help to raise public awareness of the environmental impacts caused by nitrogen (Leach, et al., 2011).

In the US, it has been shown that intervention in combustion processes, manure and fertilizer application, cropland management, nitrogen use efficiency (NUE), and wastewater treatment could reduce the anthropogenic reactive nitrogen load to the environment by 20% (Galloway & Theis, 2009). The NUE measures the extent to which the total nitrogen originally introduced into the system has been transferred into the end product. Europe can generally be considered an excess nitrogen area. Even though in Great Britain the ammoniacal nitrogen flux was reduced from 1974 to 2005 the total dissolved nitrogen flux increased due to  $\text{NO}_3^-$ ,  $\text{NO}_2^-$ , and dissolved  $\text{N}_{\text{org}}$  (Worrall, et al., 2009). In the Netherlands, approximately 40% of all nitrogen input is lost to the environment (Kroeze, et al., 2003). In Sweden, human activities have been found to disperse a major part of the nitrogen flow to the air and to water bodies (Darius & von Malmberg, 2001). A nitrogen balance was first presented for Austria for the year 1986 (Atzmüller, et al., 1990). This nitrogen budget was then evaluated from the perspective of the Austrian economy (Dissemond, et al., 1991). Subsequently, a nitrogen balance for the entire agricultural area of Austria was calculated for 1985 – 1996 in accordance with the OECD standards (OECD, 1996) and a nitrogen surplus of 30 kgN/ha was detected (Götz, 1998). The nitrogen fluxes in Austria over the period 1950 – 1995 demonstrate how anthropogenically initiated agricultural activities have interfered with

the natural nitrogen cycle and the extent to which they have affected the environment (Gaube, 2002). The most recent data on nitrogen budgets for Austria are available for the years 2001 – 2006 (Thaler, et al., 2011). Based on these data, the nitrogen budgets have been recalculated based on a diet recommended by the German Nutrition Society (DGE, 2004). Such a diet would be beneficial to human health and would substantially influence the nitrogen fluxes by allowing nitrogen to be used more efficiently. As a consequence of this change, the area needed for the production of animal-based foodstuffs, the nutritional requirements for food production, the impact on the hydrosphere, the energy demand, and the emissions of CO<sub>2</sub> equivalents would be significantly reduced (Fazeni & Steinmüller, 2011), (Thaler, et al., 2011). These potential effects have also been predicted at both European and global scales (Sutton, et al., 2011), (Stehfest, et al., 2009), (Steinfeld, et al., 2006), (Westhoek, et al., 2011).

The environmental impact of the nitrogen surplus is classically assessed based on Life Cycle Impact Assessment (LCIA). LCIA includes impact categories such as the global warming potential, eutrophication and acidification (Basset-Mens & van der Werf, 2007), (Cederberg & Flysjö, 2004), (De Vries & De Boer, 2010), (Haas, et al., 2005), (Van der Werf & Petit, 2002). EcoX indicator, for example, was defined based on LCIA. This indicator reveals the overall environmental impact of cropping systems, and it considers different chemical compounds and several impact categories, including resource depletion, land use, climate change, toxicity, acidification, and eutrophication (Brentrup, et al., 2004), (Brentrup, et al., 2004). Alternatively, the nitrogen surplus can be estimated and interpreted as an indicator of the environmental impact of cropping systems (Carpani, et al., 2008), (Ondersteijn, et al., 2001), (Schröder, et al., 2003). However, an estimate of the nitrogen surplus provides no information about the types of nitrogen compounds, their amount released to the environment, or the proportion of nitrogen lost to the atmosphere, to the hydrosphere, or to the soil. Optionally, the NUE is calculated to indicate the efficiency of agricultural production relative to total nitrogen. Moreover, the NUE provides an indication of the nitrogen surplus that will be dispersed in the environment. The worldwide NUE for cereal production has been estimated at approximately 33% (Raun & Johnson, 1999). The global NUE of industrialized countries has been increasing steadily, from 48% in 1970 and 49% in 1995 to its current value of 60%, and it is expected to reach 62% in 2030 (Bouwman, et al., 2005), (Liu, et al., 2010). Cassmann and colleagues have confirmed that the NUE of different agricultural systems can still be improved (Cassmann, et al., 2002). Despite their usefulness in facilitating the more efficient use of nitrogen and, therefore, in reducing

the effect of nitrogen on the environment, neither the nitrogen surplus nor the NUE can quantify the dispersal of various nitrogen compounds resulting from agricultural activities. However, the reported NUEs show that a significant amount of nitrogen is lost to the environment. The effects of management practices on the risk of nitrogen loss to the environment can be modeled with the Nitrogen Loss and Environmental Assessment Package model (NLEAP) (Delgado, et al., 2006), (Delgado, et al., 2008a), (Delgado, et al., 2008b). Based on the NLEAP model, a nitrogen trading tool (NTT) has been introduced in the US. The NTT can help users view the potential monetary rewards or drawbacks associated with variations in their agricultural practice (Gross, et al., 2008). However, NLEAP does not evaluate these nitrogen losses. The monetary benefit resulting from the reduction of nitrogen emissions to the environment can also be quantified with cost-benefit analysis (CBA). An example of a CBA reveals the need to prioritize  $\text{NO}_x$  and  $\text{NH}_3$  abatement over the abatement of  $\text{N}_2\text{O}$  emissions (Brink & van Grinsven, 2011). Nitrogen balances per se are among the environmental indicators for agriculture and represent one of ten different criteria for the evaluation of ecological sustainability (Austrian Ecology Organization, 2011), (Com(2001)144, 2001), (OECD, 2001a), (OECD, 2001b). However, the focus of such nitrogen balances are the emissions of single nitrogen compounds, such as  $\text{NO}_3^-$  leached into the groundwater or  $\text{NH}_3$  emissions to the atmosphere. For this reason, nitrogen balances fail to provide a holistic assessment of all nitrogen losses. In the previous chapter it has been shown that statistical entropy, applied as a measure of concentration and dilution, can potentially serve as an agri-environmental indicator.

The purpose of the present chapter is thus to use the advantages of eSEA (consideration of all N-compounds and their distribution in the different material flows) and to introduce eSEA as a new agri-environmental evaluation method, using nitrogen budgets in Austrian farming regions as an example. Two different catchments will be compared. Additionally, the nitrogen budgets for the state-of-the-art nutritional conditions in Austria are compared to those corresponding to a healthy balanced diet recommended by the German Nutrition Society.

## **3.2 Materials and methods**

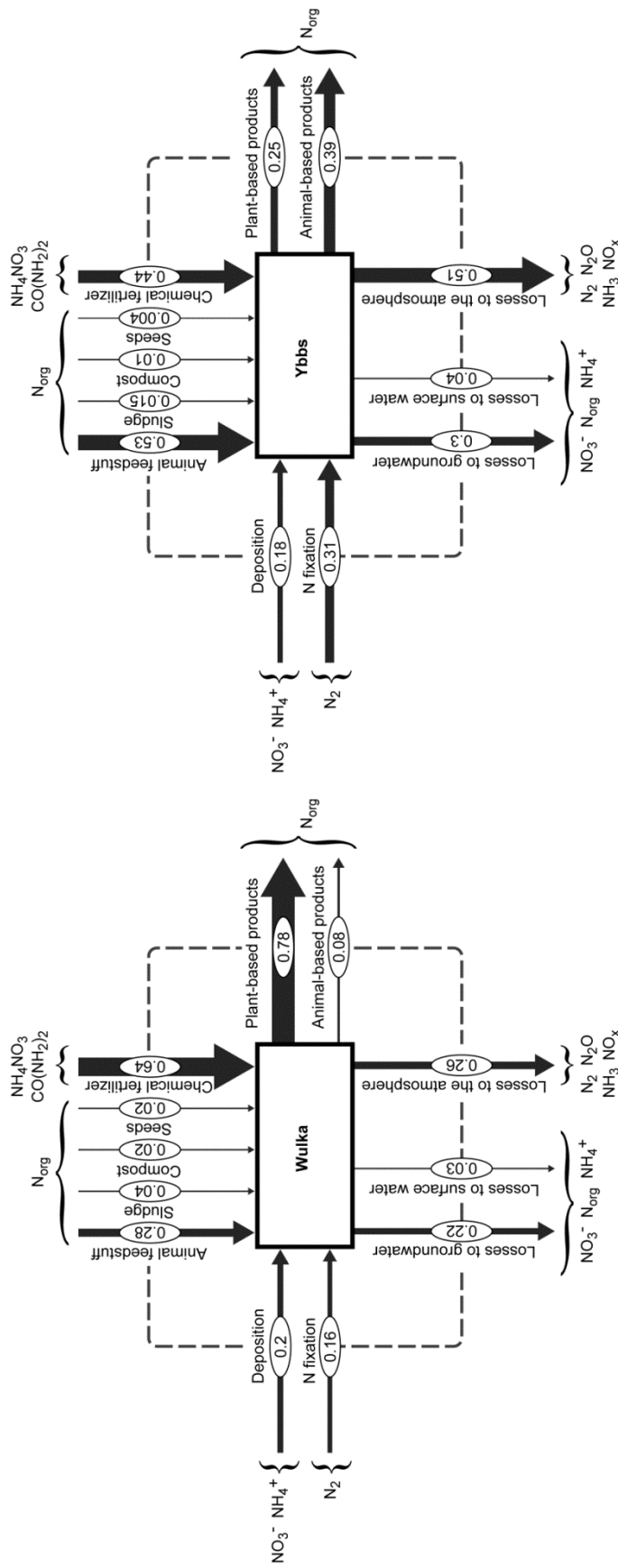
### **3.2.1 The investigated catchments**

The catchments that are the subject of this work are located in Austria. Animal husbandry and crop farming are the agricultural activities occurring in these

catchments. Nitrogen is processed through these catchments in the form of various nitrogen compounds. These compounds include  $\text{NH}_4^+$ ,  $\text{NO}_3^-$ ,  $\text{NH}_4\text{NO}_3$ ,  $\text{CO}(\text{NH}_2)_2$ ,  $\text{N}_2$ ,  $\text{NH}_3$ ,  $\text{N}_2\text{O}$ ,  $\text{NO}_x$ , and  $\text{N}_{\text{org}}$  (i.e., proteins contained in animal-based and plant-based foodstuffs) and are distributed by different material flows (e.g., fertilizer, seeds, compost, water, air). Food products based on  $\text{N}_{\text{org}}$  are extracted, and by-products (gaseous N emissions such as  $\text{N}_2\text{O}$  or  $\text{NH}_3$  or waterborne emissions such as  $\text{NO}_3^-$ ) are released into the atmosphere and hydrosphere. Nitrogen can also be stored in the soil. Extensive data sets are available for two Austrian catchments and for two nutritional alternatives, the nutritional state-of-the-art for all Austria (ASN) and the optimized diet for Austria (AON) according to the German Nutrition Society (Thaler, et al., 2011). The data are expressed as average annual values over the period 2001 – 2006. To apply eSEA, the following additional assumptions are required: animal feedstuff is assumed to contain 50% dry matter, and chemical fertilizer is assumed to represent a mixture of 94%  $\text{NH}_4\text{NO}_3$  and 6%  $\text{CO}(\text{NH}_2)_2$  with a total nitrogen content of 40%. The value of deposition is assessed from the precipitation data for the period 2001 – 2006 (Parajka, et al., 2007). Sludge is estimated to include a total nitrogen content of 1.5%. A dry matter content of 10% is assumed for forage and a 50% dry matter content for farm fertilizer. The  $\text{N}_{\text{org}}$  representing protein in animal-based products is not differentiated from the  $\text{N}_{\text{org}}$  in plant-based products.

The data for the two Austrian regions considered in the study are then normalized to 1 kg nitrogen anthropogenic input. This input includes nitrogen from animal feedstuffs, sludge, compost, chemical fertilizer, and seeds. In this way, the regions can be compared to each other. The data for the ASN system are normalized to 4.4 kgN/cap/yr, which corresponds to the actual nitrogen uptake in Austria. The data for the AON system are normalized to a nitrogen uptake of 4.0 kgN/cap/yr. This value corresponds to the reduced nitrogen uptake resulting from the optimized diet defined by the German Nutrition Society. Both systems, ASN and AON, are thus normalized to produce sufficient nitrogen for human demand and can be compared to one another on this basis.

3.2.1.1 The Wulka and the Ybbs catchments

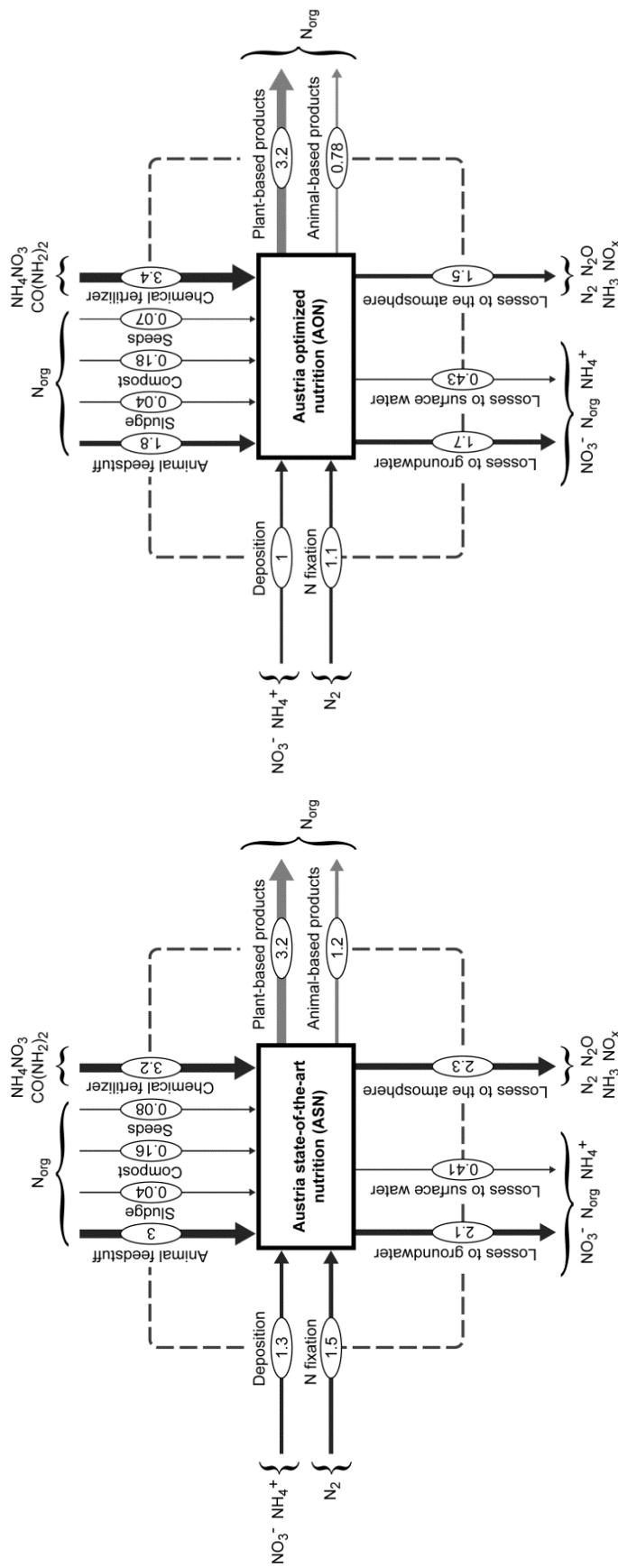


**Figure 3.1:** Nitrogen budgets including the individual nitrogen compounds; data are normalized to 1 kg nitrogen anthropogenic input. Left: the Wulka catchment in Burgenland (eastern Austria); Right: the Ybbs catchment in Lower Austria (northern Austria)

The Wulka catchment is located in the federal state of Burgenland, in eastern Austria, and covers 38,333 ha. The area used for agriculture during 2001 – 2006 was 19,349 ha. A total of 57 kgN/ha/yr (39 kgN/cap/yr) are processed in Wulka. A total of 64% of the anthropogenic nitrogen enters the region via chemical fertilizer, and 28% of the anthropogenic nitrogen results from animal feedstuffs. The dominant production of nitrogen in the region is represented by plant-based goods. The NUE is 63%. Consequently, the N surplus in Wulka is 37%, i.e., 21 kgN/ha/yr. The nitrogen budget is shown on the left side of Figure 3.1, where the individual nitrogen compounds that are contained in the different material flows are also specified.

The Ybbs catchment is located in the federal state of Lower Austria, in northern Austria, and covers 110,468 ha. The area used for agriculture during 2001 – 2006 was 38,107 ha. The Ybbs catchment experiences a nitrogen turnover of 138 kgN/ha/yr (76 kgN/cap/yr). In all, 44% of the introduced nitrogen comes from chemical fertilizer and 53% from animal feedstuffs. In Ybbs, the animal-based products are dominant. Less nitrogen is generated in the form of plant-based products in Ybbs than in Wulka. In Ybbs, the nitrogen emissions to groundwater are greater and the nitrogen emissions to the atmosphere substantially higher. The NUE is 43%. Consequently, the nitrogen surplus in Ybbs is 57%, i.e., 79 kgN/ha/yr. The nitrogen budget is shown on the right side of Figure 3.1.

3.2.1.2 The “Austria state-of-the-art nutrition” and the “Austria optimized nutrition” systems



**Figure 3.2:** Left Nitrogen budgets for the ASN system; flows are normalized to a nitrogen uptake of one person per year (4.4 kgN/cap/yr). Right: nitrogen budgets for the AON system; flows are normalized to an optimal nitrogen uptake of one person per year (4.0 kgN/cap/yr).



The estimated total area of Austria is 8,387,100 ha. Of this area, 222,775 ha were used for agriculture during 2001 – 2006. The nitrogen turnover is 99 kgN/ha/yr or 39 kgN/cap/yr. The NUE is 48%. The nitrogen surplus in Austria is 52%, i.e., 51 kgN/ha/yr. The nitrogen budget is shown on the left side of Figure 3.2.

The German Nutrition Society has recommended a nutrition plan that would primarily benefit human health (DGE, 2004). Under this nutrition plan, the nitrogen budgets in Austria would change (cf. right side of Figure 2). The total nitrogen turnover would be reduced to 71 kgN/ha/yr (corresponding to 28 kgN/cap/yr). In all, 35% less nitrogen would be converted to animal-based goods. Therefore, 40% less nitrogen would be needed in the form of animal feedstuffs. Consequently, the gaseous nitrogen losses would decrease by 35%. The nitrogen losses to groundwater would decrease by 19%. The NUE for the AON system would increase to 53%. Consequently, the nitrogen surplus would decrease to 33 kgN/ha/yr. The nitrogen budget is shown on the right side of Figure 3.2.

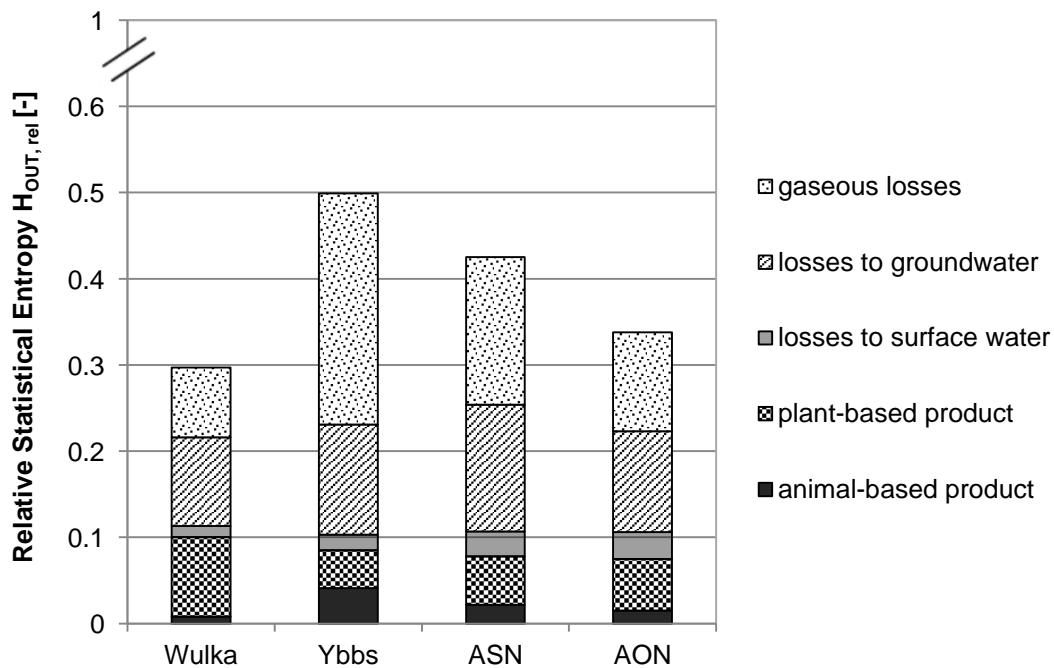
### 3.3 Results and discussion

#### 3.3.1 Evaluation of the nitrogen performance of the Wulka and the Ybbs catchments and of the Austria state-of-the-art-nutrition (ASN) and the Austria optimized nutrition (AON) system

In this chapter, the nitrogen performances of the Wulka and Ybbs catchments, of the entire ASN and of the AON systems are assessed with eSEA. The numerical results of this assessment are shown in Table 3-1 and are illustrated in Figure 3.3. To better understand the meaning of the entropy values, two contrasting hypothetical reference situations are presented: if all nitrogen is transformed to food products in the catchment, entropy production is minimized ( $H_{\min}$ ); in contrast, entropy generation is maximized ( $H_{\max}$ ) if all nitrogen is emitted to the environmental compartment with the lowest natural background concentration (this outcome would correspond to the emission of  $N_{\text{org}}$  to groundwater of very high water quality according to the Austrian Water Act (BGBl II Nr, 98/2010)).

**Table 3-1:** Calculation of the maximum statistical entropy  $H_{MAX}$ .

	$H_{IN}$	$H_{min}$	$H_{OUT}$	$H_{max}$	$H_{IN,rel}$	$H_{min,rel}$	$H_{OUT,rel}$	$\Delta H$	NUE
<b>WULKA</b>	4.27	6.43	12.0	40.4	0.11	0.16	0.30	<b>180%</b>	63%
<b>YBBS</b>	4.63	8.04	20.1		0.11	0.20	0.50	<b>335%</b>	43%
<b>ASN</b>	4.02	6.59	17.2		0.10	0.16	0.42	<b>327%</b>	48%
<b>AON</b>	4.01	6.93	13.6		0.10	0.17	0.34	<b>240%</b>	53%

**Figure 3.3:** eSEA results for the nitrogen performances of the Wulka catchment, the Ybbs catchment, the ASN system, and the AON system

The entropy increase  $\Delta H$  is significantly higher for the Ybbs catchment (335%) than for the Wulka catchment (180%). This result shows that the nitrogen anthropogenically applied to the system is diluted to a greater extent in Ybbs than in Wulka. Figure 3.3 shows that the principal contributors, by far, to the poor nitrogen performance of the Ybbs catchment are the gaseous losses to the atmosphere. The amount of nitrogen emitted to the atmosphere by the Ybbs catchment is almost twice that emitted by Wulka. The entropy contribution of the gaseous nitrogen losses is, however, 3.3-fold higher for Ybbs than for Wulka, based on the various N compounds (e.g.,  $\text{NH}_3$ ,  $\text{N}_2\text{O}$ , and  $\text{NO}_x$ ), their individual background concentrations, and the various diluting masses. Nitrogen losses to both the surface water and the groundwater also marginally produce

an increased entropy value in the Ybbs catchment. The nitrogen that is converted into the products is not diluted; however, the creation of the products also generates entropy to a certain extent. The entropy proportion associated with the products is in the range of the input entropy ( $H_{rel}=0.1$ ) for the Wulka catchment and is slightly less than the corresponding input entropy for the Ybbs catchment. This difference is due primarily to the lower concentration of nitrogen associated with plant-based products. Accordingly, Ybbs achieves a higher concentration of N relative to the food products, but this result is achieved at the cost of the high dilution of nitrogen compounds in the atmosphere (cf. Figure 3.1). In general, the entropy production associated with the food products is higher for Wulka than for Ybbs, but the entropy generation due to the losses of nitrogen to the environment is disproportionately higher for Ybbs. An explanation of this outcome cannot be derived directly from the available data. However, according to literature findings, the production of animal-based foods might be the most likely explanation for the greater losses from the Ybbs catchment (Thaler, et al., 2011), (Fazeni & Steinmüller, 2011), (Stehfest, et al., 2009), (Steinfeld, et al., 2006), (Sutton, et al., 2011), (Westhoek, et al., 2011). It may also be possible to improve the state-of-the-art nitrogen management of the Ybbs catchment to allow the same amount of animal-based goods to be produced in a way that decreases the emissions to the atmosphere. The NUE indicates a higher efficiency for Wulka (63%) than for Ybbs (43%). However, changes in the gaseous nitrogen losses ( $N_2$ ,  $NH_3$ ,  $N_2O$ ,  $NO_x$ ) or the nitrogen emissions to surface water and groundwater ( $NO_3^-$ ,  $NH_4^+$ ,  $N_{org}$ ) would not be reflected in the NUE. If, for example, the  $NH_3$  emissions were reduced, the statistical entropy would decrease. The same outcome would occur, for example, as a result of a reduction of the  $NO_3^-$  discharge to surface water and groundwater. The NUE would not react to such changes. The disadvantages of the NUE are discussed in more detail in section 3.3.2.

The entropy increase,  $\Delta H$ , is significantly higher for the ASN system (327%) than for the AON system (240%). Both systems produce sufficient nitrogen to meet the human demand. Overall, however, the AON system dilutes nitrogen to a lesser extent than the ASN system. Figure 3.3 shows that reduced gaseous losses and decreased emissions to groundwater are primarily responsible for the improved nitrogen performance of the AON system. The nitrogen losses to surface water and the associated entropy proportions are comparable in the two systems (cf. Figure 3.2). The ASN system transfers 1.5 times as much nitrogen to animal-based foodstuffs and emits 1.5 times as much nitrogen to the atmosphere as the AON system. Consequently, the entropy

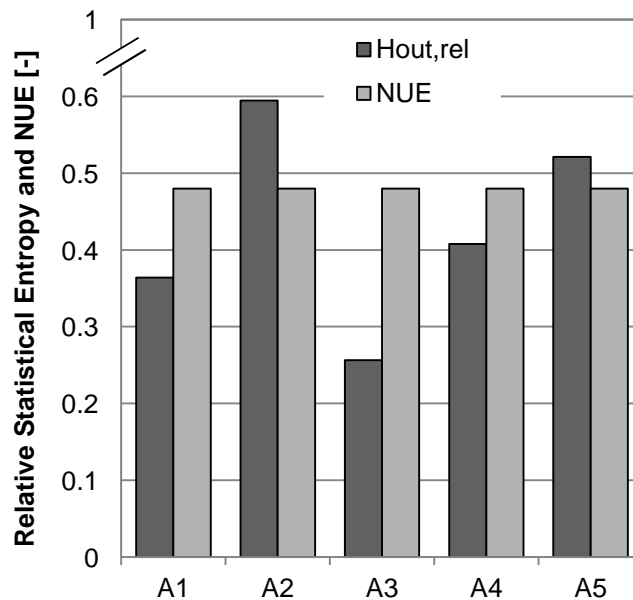
proportion of the animal-based foods in the ASN system is 1.5-times greater than the corresponding entropy proportion in the AON system, whereas the entropy production associated with the plant-based products is slightly lower (6.3%). The NUE analysis confirms an increased efficiency for the AON system (53% compared to 48% for the ASN system). However, the response of the NUE to the alteration of the N budgets is less significant than that of the statistical entropy.

To present a comprehensive discussion of the nitrogen budgets of both regions, the ecological rucksack of the nitrogen input flows must also be considered. This parameter would include the exploitation of the resources needed for the production and transport of the particular material flows. The ecological rucksack of animal feedstuffs is more complex and can be significantly larger than that one of chemical fertilizer, for instance. The ASN system requires 1.9 times more animal feedstuffs than the AON system. Therefore, the total input of fertilizer for the ASN alternative would be greater. However, the different ecological rucksacks associated with the material flows that are responsible for the nitrogen input are not considered in this evaluation. Moreover, the detailed nutritional requirements and the energy demands of both regions are not incorporated. Furthermore, the particular hydrological and geological conditions associated with the catchments can limit the resulting nitrogen performance and should therefore be considered in the discussion. These considerations are not addressed in this context because the focus is the application of eSEA to the assessment of nitrogen performance rather than a comprehensive study of the catchments.

### **3.3.2 Emission scenarios**

To emphasize the benefits that favor the use of eSEA rather than NUE, several hypothetical emissions scenarios have been developed. These scenarios are based on the ASN system and will be evaluated with both the eSEA and NUE approaches. Scenario A1 is defined by the original nitrogen budgets in the ASN system. In both scenarios A2 and A3, the total nitrogen losses to the atmosphere are kept constant, but the emissions of the different nitrogen compounds ( $N_2$ ,  $NH_3$ ,  $NO_x$  and  $N_2O$ ) are allowed to vary. In scenario A2, the emissions of  $NH_3$ ,  $NO_x$ , and  $N_2O$  are each increased by 50%, whereas  $N_2$  is reduced accordingly. In scenario A3, only  $N_2$  is emitted to the atmosphere. In both scenarios A4 and A5, the nitrogen losses to surface water and groundwater are kept constant, but the emissions of  $NO_3^-$ ,  $NH_4^+$  and  $N_{org}$  are modified. For scenario A4, it is assumed that only  $NO_3^-$  is lost to surface water and groundwater.

In scenario A5, the nitrogen losses to the hydrosphere are assumed to occur only in the form of  $N_{org}$  only. The relative entropy values for the output distribution of the nitrogen compounds and the NUEs are shown in Figure 3.4.

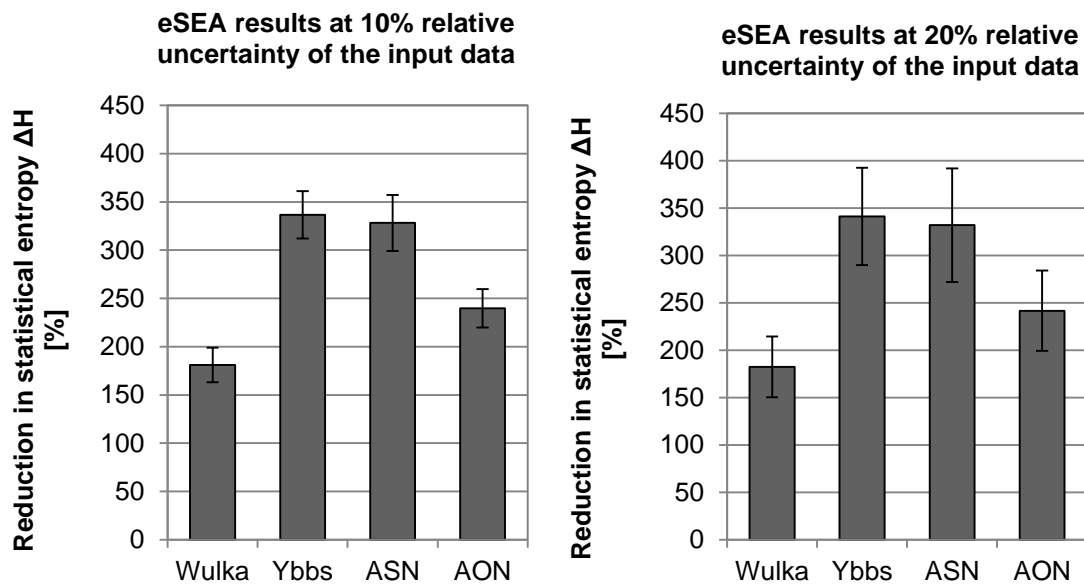


**Figure 3.4:** eSEA results and NUEs for the hypothetical emission scenarios based on the ASN system

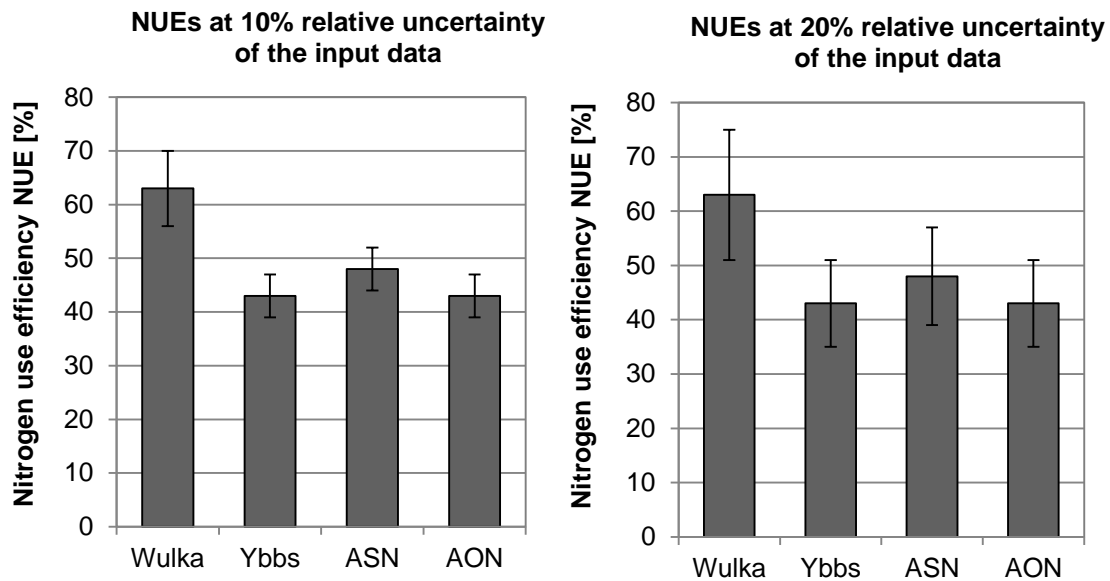
Figure 3.4 clearly shows that only eSEA responds to the presented hypothetical emission scenarios. The NUE remains the same for all scenarios because it only considers the total nitrogen in the product and in the input. However, the additional emissions of  $NH_3$ ,  $NO_x$ , and  $N_2O$  to the atmosphere in scenario A2, for example, are clearly less desirable. In turn, it is favorable if all nitrogen losses to the atmosphere occur in the form of  $N_2$  (cf. scenario A3). The natural background concentration of  $NO_3^-$  in water bodies of very high water quality is significantly higher than the concentration of  $N_{org}$ . As a result, the discharge of  $NO_3^-$  produces less entropy and, accordingly, less dilution than the discharge of  $N_{org}$ . The environmental impact of  $NO_3^-$  on water bodies is also demonstrably lower than the impact of  $N_{org}$  (BGBI II Nr, 461/2010), (Guinée, et al., 2002), (Westgate & Park, 2010). These results demonstrate that NUE might not be appropriate for a comprehensive assessment of nitrogen budgets, and the evaluation of these budgets may benefit from the use of eSEA.

### 3.3.3 Sensitivity analysis

A sensitivity analysis for the eSEA results and the NUEs is presented based on a Monte Carlo simulation. Many input data show an uncertainty of approximately  $\pm 10\%$  (Danius, 2002). Due to missing information about the quality of the available data used in this work, the relative uncertainty is assumed to have values of 10% or 20%. These two cases are analyzed on the assumption of normally distributed data. The mean values for the changes in statistical entropy and NUE along with the corresponding standard deviations are shown in Figures 3.5 and 3.6.



**Figure 3.5:** Results for eSEA obtained from a sensitivity analysis based on relative uncertainty levels of the input data of 10% (left) and 20% (right)



**Figure 3.6:** NUEs obtained from a sensitivity analysis based on relative uncertainty levels of the input data of 10% (left) and 20% (right); results for eSEA obtained from a sensitivity analysis based on relative uncertainty levels of the input data of 10% (left) and 20% (right)

The results in Figures 3.5 and 3.6 show that the change in statistical entropy is significantly lower for the Wulka catchment than for the Ybbs catchment even at relative data uncertainties of 20%. Based on a relative data uncertainty of 10%, the AON system still clearly achieves an improvement in nitrogen performance. The certainty that the AON system will result in improved nitrogen performance is slightly reduced if a relative data uncertainty of 20% is assumed. The NUE approach indicates that the nitrogen performance of the Wulka catchment is superior to that of the Ybbs catchment even if the data are associated with a 20% relative uncertainty. However, greater efficiency of the AON system is no longer significant if an input data uncertainty of 10% or 20% is considered. Based on these results, the NUE value is considerably less meaningful. However, it has previously been demonstrated that the AON system is more advantageous for the environment in many respects than the ASN system (Fazeni & Steinmüller, 2011), (Thaler, et al., 2011).

### 3.4 Conclusions

In this chapter, the usefulness of statistical entropy as an agri-environmental indicator was tested by applying eSEA to the nitrogen budgets of two Austrian regions, the Wulka and the Ybbs catchments, and to the ASN and AON systems. The results show

that the nitrogen performance of the Wulka catchment is superior to the nitrogen performance of the Ybbs catchment, primarily as a result of the lower level of nitrogen emissions of the former to the atmosphere and to groundwater. The use of the optimized nutrition system defined by the German Nutrition Society changes the Austrian nitrogen budgets so that the total nitrogen is diluted to a lesser extent. These changes improve the Austrian nitrogen performance. However, the significance of the results must be considered in view of the expected uncertainty in the data. The NUEs for the Wulka catchment is greater than that for the Ybbs catchment; however, if the expected uncertainty of the input data is considered, the AON system is not clearly more efficient than the ASN system. Furthermore, variations in the nitrogen compounds released to the atmosphere and in those discharged to surface water and groundwater are not addressed by the NUE calculations. Therefore, we conclude that statistical entropy is a more comprehensive indicator for assessing nutrient balances than NUE. Finally, it is recommended to use eSEA for the assessment of the nitrogen budgets of other systems for further testing of the approach and after successful validation propose the integration of eSEA results in decision-making processes regarding nitrogen management strategies.



## **4 Extended statistical entropy analysis for improving evaluation of wastewater treatment plants**

### **Abstract**

Extended statistical entropy analysis (eSEA) is used to evaluate the nitrogen budgets of 56 Austrian WWTPs. The eSEA results are then compared to the WWTPs specific nitrogen removal rates. Among 5 WWTPs that achieve a removal rate of 75% the eSEA detects significant differences in the nitrogen performance. The main reason for this is that eSEA considers all nitrogen species and seems to be more discriminating than the nitrogen removal rate. Additionally, the energy consumption and the costs of the mechanical-biological treatment process are related to the nitrogen performance according to the eSEA. The influence of the WWTP size on the energy-efficiency and cost-effectiveness of the nitrogen treatment is investigated. Results indicate that energy-efficiency does not necessarily coincide with cost-effectiveness. In this chapter, it is shown that smaller WWTPs between 22,000 PE and 50,000 PE can be operated as energy-efficiently as larger WWTPs between 100,000 and 1,000,000 PE. On average, the smaller plants operate less cost-effective than the large ones. This research offers a new method for the assessment of the nitrogen performance of WWTPs, and suggests that small WWTPs are not necessarily less energy-efficient and cost-effective than large ones.

### **4.1 Introduction**

The cleaning performance of WWTPs is expressed by removal rates (e.g. of nitrogen or phosphorus). There are also mandatory emission limits, such as an nitrogen removal rate in excess of 70% at temperatures  $> 12\text{ }^{\circ}\text{C}$  for all WWTPs greater than 5,000 PE as well as an  $\text{NH}_4^+$  concentration of less than 5 mgN/L (Phillippitsch & Grath, 2006), (Thaler, 2009). The advantage of using the nitrogen removal rate as a measure of cleaning performance is that it can be easily calculated. The determination of the N-compounds is reduced to the  $\text{N}_{\text{total}}$  in the influent and effluent. However, in this determination, nitrogen is not differentiated in its various chemical species (e.g.,  $\text{NH}_4^+$ ,  $\text{NO}_3^-$ ,  $\text{N}_2$  etc.); thus,  $\text{NH}_4^+$  and  $\text{NO}_3^-$  are treated equally, although the environmental impact of these two forms of nitrogen are different. The Austrian Water Act and Life Cycle Impact Assessment (LCIA) assign individual nitrogen compounds different emission limits and impact factors (BGBl II Nr, 98/2010), (BGBl II Nr, 99/2010), (BGBl II

Nr, 461/2010), (Guinée, et al., 2002)). For example,  $\text{NH}_4^+$  has a higher ecotoxicological impact on water bodies than  $\text{NO}_3^-$ . Other studies have concluded that the role and fate of aquatic  $\text{N}_{\text{org}}$  is still unknown, which implies that  $\text{N}_{\text{org}}$  in water bodies cannot be regarded as  $\text{NH}_4^+$  (Westgate & Park, 2010).  $\text{N}_2\text{O}$  plays a major role in global warming (Kampschreur, et al., 2009). The omission of gaseous nitrogen compounds is a drawback of the use of the nitrogen removal rate, because wastewater purification can result in atmospheric pollution (e.g., the emission of  $\text{N}_2\text{O}$  and  $\text{NH}_3$ ). Wang and colleagues have stressed the problem of limited integration of  $\text{N}_2\text{O}$  emissions from WWT into the overall nitrogen pollution reduction, and propose creation of a greenhouse gas crediting system (Wang, et al., 2011).

In Austria, a performance indicator (“Leistungskennwert”: LW) has been developed to describe the cleaning capacity of WWTPs that considers the effluent concentrations of  $\text{NH}_4^+$  and  $\text{NO}_3^-$ . Specific weighting factors are assigned to each emission concentration (Spatzierer, et al., 2000). Other nitrogen compounds in the effluent, such as  $\text{N}_{\text{org}}$ , gaseous N-emissions such as  $\text{N}_2\text{O}$ , and nitrogen transfer to sludge, are ignored.

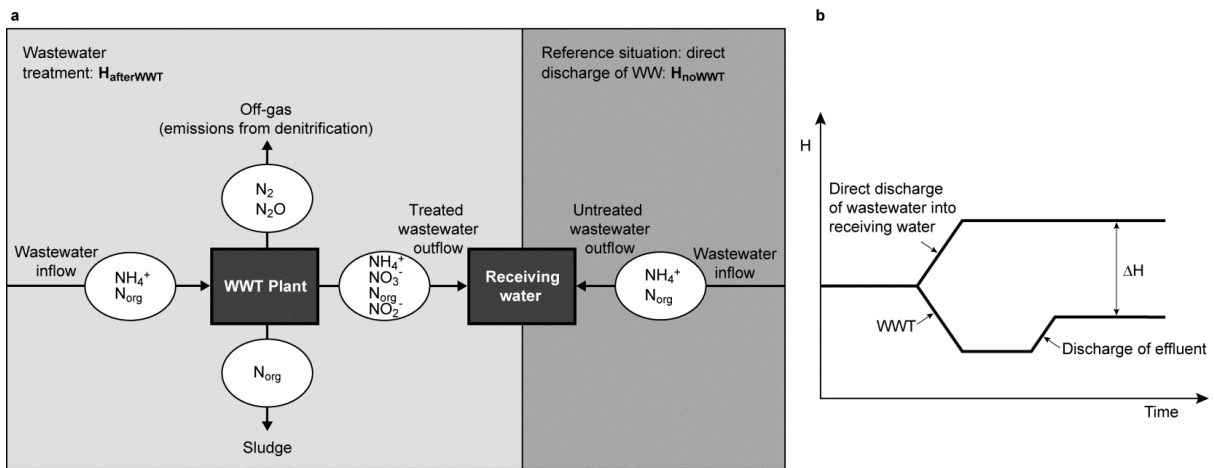
An effluent quality index (EQ) is utilized in the Benchmarking Simulation Model. This index distinguishes the effluent concentrations of Kjeldal-N ( $\text{NH}_4^+ + \text{N}_{\text{org}}$ ) and  $\text{NO}_3^-$ ; in addition, in its revised form, this index assigns different weighting factors to both nitrogen concentration terms, which permits their individual eco-toxicological potentials to be considered (Vanrolleghem, et al., 1996), (Nopens, et al., 2010). However, no differentiation between  $\text{NH}_4^+$  and  $\text{N}_{\text{org}}$  is made, and the gaseous nitrogen emissions and the nitrogen that is transferred to the sludge are not included in the index. Therefore, in this chapter eSEA is used for the evaluation of the nitrogen performance of Austrian WWTPs.

The energy budgets and costs of WWTPs have been studied extensively. Both metrics are usually referred to the pollution load of the wastewater, expressed by PE. According to state-of-the-art literature, large WWTPs (>100,000 PE) are able to operate more energy- and cost-efficiently than small plants (Agis, 2002), (Nowak, 2002), (Lindtner, et al., 2008), (Kroiss & Svardal, 2009), (Hernandez-Sancho & Sala-Garrido, 2009), (Lindtner, 2010). In this chapter, both energy consumption and costs are related to the nitrogen performance as assessed by eSEA and the influence of the size of WWTPs for energy-efficiency and cost-effectiveness of the nitrogen performance is investigated.

## 4.2 Methods

### 4.2.1 Application of eSEA for the assessment of the N-removal performance of WWTPs

In this chapter eSEA is applied to evaluate the N-removal performance of Austrian WWTPs. First, a nitrogen mass balance must be established: assuming that there is no storage of nitrogen in the WWTP, the incoming nitrogen must equal the nitrogen that leaves the WWTP. Figure 4.1a illustrates the flow of nitrogen compounds before and after WWT assuming the state-of-the-art biological treatment including both nitrification and denitrification. Figure 4.1b illustrates the effect of wastewater treatment according to statistical entropy.



**Figure 4.1:** Description of the nitrogen treatment by means of statistical entropy **(a)** Left: Schematic illustration of nitrogen compounds through the WWT process; Right: Reference situation: the wastewater is discharged without treatment into the receiving waters. **(b)** The direct discharge of wastewater to the hydrosphere results in an entropy increase. WWT reduces the entropy, and the discharge of the effluent to the receiving water results in a (small) increase.  $\Delta H$  quantifies the cleaning performance of the WWT process. **(c)** Results for eSEA obtained from a sensitivity analysis based on relative uncertainty levels of the input data of 10% (left) and 20% (right)

The emission of every single nitrogen compound as described in Figure 4.1a will result in a dilution process in both the receiving waters and the atmosphere (i.e., the environmental compartments). The dilution of the nitrogen in the sludge is not considered because the sludge may be further processed. The water or air mass that dilutes a nitrogen emission depends on both the emission concentration and the concentration of the respective nitrogen compound in the receiving environmental compartment. For example, surface waters with a good ecological status contain

approximately 1 mgN/L of  $\text{NO}_3^-$  (BGBl II Nr, 461/2010). Thus, the emission of 1 mgN- $\text{NO}_3^-$ /L does not contribute to the statistical entropy, but an emission of 10 mgN- $\text{NO}_3^-$ /L produces entropy. A detailed mathematical description of eSEA can be found in Chapter 2. The calculation of the statistical entropy of nitrogen compounds is additionally outlined in Table 4-1.

**Table 4-1:** Brief overview of the computation of the statistical entropy of nitrogen compounds in WWTPs

Step 1: measured data	$\dot{M}_i, c_{im}, c_{im,geog}$
Step 2: normalization of the mass flow	$m_{im} = \frac{\dot{M}_i}{\sum_i \sum_m \dot{X}_{im}} \text{ (Eq.4.1)}$ <p>Where <math>\dot{X}_{im} = \dot{M}_i * c_{im}</math> (Eq.4.2)</p>
Step 3: calculation of the diluting masses of each N-compound	$m'_{im} = m_i * \frac{c_{im} - c_{im,geog}}{c_{im,geog}} * 100 + m_i \text{ (Eq.4.3)}$ <p>and <math>c'_{im} = \frac{c_{im} * c_{im,geog}}{c_{im} - 0.99 * c_{im,geog}} * 0.01 \text{ (Eq.4.4)}</math></p>
Step 4: computation of the statistical entropy	$H(m'_{im}, c'_{im}) = - \sum_i \sum_m m'_{im} * c'_{im} * \log_2(c'_{im}) \text{ (Eq.4.5)}$

$\dot{M}_i$  is the measured mass flow in kg per day. The index i refers to the wastewater, effluent, off-gas, sludge, and the environmental compartments air and water. The variable  $c_{im}$  (in kgN/kg) corresponds to the measured concentration of a nitrogen compound in the particular mass flow i. The nitrogen compounds ( $\text{NO}_3^-$ ,  $\text{NH}_4^+$ , etc.) are indexed by m. The background concentration of a compound m in an environmental compartment i is indicated by the variable  $c_{im,geog}$ . The mass flows are normalized according to Equation 4.1. The denominator of Equation 1 equals the total flow of nitrogen through the WWTP such that the masses  $m_i$  are related to one mass-unit of nitrogen (e.g., kg in the effluent per kg of the total nitrogen throughput). Normalization is required to make processes of different size comparable. In the next step, the diluting mass  $m'_{im}$  and the corresponding concentration term  $c'_{im}$  are calculated according to Equation 4.3 and Equation 4.4, respectively. The mass-function calculates how much mass in the water or air is needed to dilute the emitted concentration to its corresponding background concentration. The dimensionless mass-function for the nitrogen in the sludge is computed according to Equation 4.1. The statistical entropy H is then calculated according to Equation 4.5 for every nitrogen compound in the

effluent, the atmosphere and the sludge. Thus, the statistical entropy is a function of the mass flows, such as the wastewater, effluent, air and sludge, the emission concentrations and the corresponding background concentrations of all nitrogen compounds. More diluted mass flows and larger differences between the emitted and the background concentrations result in higher entropy values and, consequently, increased dilution in the environment. Given the assumption that dilution should be avoided whenever possible for sustainable resource management, low entropy values are desired. The entropy values of all emitted nitrogen compounds are added to obtain the total statistical entropy of nitrogen after WWT ( $H_{\text{afterWWT}}$ ). This value is compared with the statistical entropy determined for a hypothetical scenario in which the untreated wastewater is directly discharged into the receiving waters ( $H_{\text{noWWT}}$ ). The benefit of a WWTP for nitrogen treatment is then expressed as the reduction in the statistical entropy ( $\Delta H$ ) relative to the direct discharge of wastewater into receiving waters (see Figure 4.1b). A higher  $\Delta H$  value indicates a more favorable performance of a particular WWTP because it results in lower dilution of nitrogen compounds and thus, fewer losses to the environment. The main advantage of eSEA for the assessment of the nitrogen performance of WWTPs is that all nitrogen compounds, as well as the flows of wastewater, effluent and sludge, can be considered both qualitatively and quantitatively. The environmental impact is reflected in the quantification of the dilution. Thus, a comprehensive evaluation of the nitrogen performance of a WWTP can be provided by this analysis. The disadvantages of eSEA are the relatively large data requirement, the inability to perform the calculation with a single equation, in contrast to the estimation of the nitrogen removal rate, and the lack of other studies that can be used to compare the results.

#### **4.2.2 Data of Austrian WWTPs**

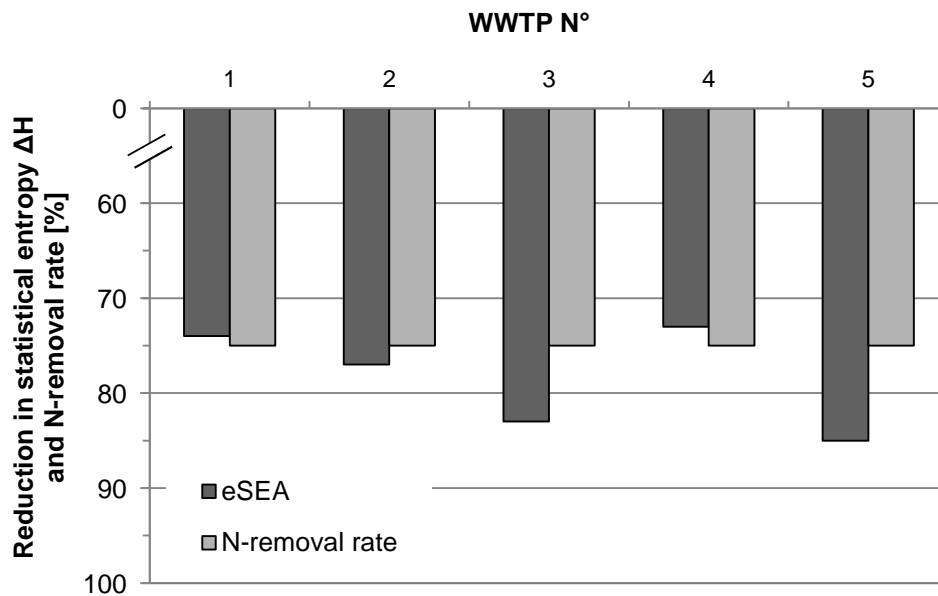
The annual average values of the concentrations and respective fractions of  $\text{NH}_4^+$ ,  $\text{NO}_3^-$  and  $\text{N}_{\text{total}}$  in the wastewater and the effluent, the wastewater inflow, the sludge volumes and the amount of nitrogen in the sludge are available for 56 Austrian WWTPs. All of these WWTPs use both nitrification and denitrification processes and meet mandatory emission standards (Phillippitsch & Grath, 2006). The data for each WWTP are measured in their respective laboratories according to German standards. Because gaseous emissions are not directly measured, the  $\text{N}_2\text{O}$  emissions of each WWTP are estimated to be 0.5% of the total nitrogen input (based on an Austrian study), and the  $\text{N}_2$  amount is estimated from the nitrogen mass balance (Kroiss, et al., 2007). For each

plant, the energy consumptions (in kWh) and the total operating costs (in EUR) of the mechanical-biological treatment process are available. The operating costs include the costs for labor, energy, external services, and additional materials, as well as other costs. The mean atmospheric background concentrations used in this paper were obtained from the ESPERE Climate Encyclopedia (Uherek, 2004). Both the  $\text{NO}_3^-$  and  $\text{NH}_4^+$  background concentrations in the surface and ground water are set in accordance with a very good ecological status of the water (BGBl II Nr, 98/2010), (BGBl II Nr, 99/2010), (BGBl II Nr, 461/2010).  $\text{N}_{\text{org}}$  is hardly present in the hydrosphere; thus its background concentration is assumed to be approximately four orders of magnitude smaller than the background concentration of  $\text{NH}_4^+$ .

## **4.3 Results and discussion**

### **4.3.1 Assessment of the Nitrogen performance of WWTPs: eSEA vs. nitrogen removal rate**

In Figure 4.2 the nitrogen performance of 5 selected Austrian WWTPs according to both the reduction in statistical entropy ( $\Delta H$ ) and the nitrogen removal rate is shown. The scaling for both indicators is between 0% and 100%, where 0% refers to the absence of nitrogen removal, i.e., the discharge of untreated wastewater (thus the complete load of nitrogen in the wastewater) into the receiving waters. A 100% removal rate describes a hypothetical situation in which all of the nitrogen compounds in the wastewater are removed. A 100% eSEA performance result indicates that the WWT process transforms all of the nitrogen compounds in the wastewater to either harmless nitrogen species, such as  $\text{N}_2$ , which has a high natural background concentration in the atmosphere or concentrates the nitrogen in the sludge. Both situations (0% and 100%) are not realistic, but serve as a reference.



**Figure 4.2:** Assessment of the nitrogen performance of five selected Austrian WWTPs based on eSEA and the nitrogen removal rate.

All of the WWTPs report nitrogen removal rates of ca 75%. Consequently, these plants would be considered to exhibit equally good cleaning performance. The eSEA results, however, reveal that there are differences in the nitrogen performance of the individual WWTPs. WWTP N°5 achieves the highest reduction in statistical entropy ( $\Delta H=85\%$ ) and is thus the most favorable. WWTP N°4 is the least favorable, with a  $\Delta H$  of 73%. WWTP N°1 achieves a  $\Delta H$  of 74%, WWTP N°2 has a  $\Delta H$  of 77%, and WWTP N°3 attains a  $\Delta H$  of 83%. In Table 4-2 the proportion of each nitrogen compound in the total nitrogen amount and its contribution to the statistical entropy after WWT ( $H_{\text{afterWWT}}$ ), which has a direct influence on the reduction in the statistical entropy  $\Delta H$ , are summarized.

**Table 4-2:** Proportion of nitrogen compounds to the total nitrogen after WWT and contribution of the individual nitrogen compounds to the statistical entropy after WWT for five Austrian WWTPs.

	WWTP N°1	WWTP N°2	WWTP N°3	WWTP N°4	WWTP N°5
<b>Proportion of nitrogen compounds to total nitrogen after WWT [%]</b>					
NH <sub>4</sub> <sup>+</sup> , aq.	3	10	2	2	1
NO <sub>3</sub> <sup>-</sup> , aq.	16	15	6	5	9
N <sub>org</sub> , aq.	6	0	6	15	5
N <sub>2</sub> , gas.	53	63	65	56	74
N <sub>2</sub> O, gas.	0.5	0.5	0.5	0.5	0.5
N <sub>org</sub> , sludge	21	12	21	21	11
<b>Contribution of the nitrogen compounds to the statistical entropy after WWT (H<sub>afterWWT</sub>) [%]</b>					
NH <sub>4</sub> <sup>+</sup> , aq.	11	39	14	9	5
NO <sub>3</sub> <sup>-</sup> , aq.	45	49	23	14	46
N <sub>org</sub> , aq.	28	0	40	63	39
N <sub>2</sub> , gas.	0.2	0.3	0.2	0.3	0.3
N <sub>2</sub> O, gas.	3	3	4	3	4
N <sub>org</sub> , sludge	13	9	19	11	6

WWTP N°4 emits more nitrogen in the form of N<sub>org</sub> in the effluent to the river (15%) than does WWTP N°5 (5%). N<sub>org</sub> represents a composition of various organic compounds that are naturally present in scarce quantities in rivers with a good ecological status. N<sub>org</sub> is therefore the main contributor to the statistical entropy after WWT by WWTP N°4. WWTP N°5 achieves a higher denitrification rate because most of the nitrogen is emitted as N<sub>2</sub> (74%). By contrast, only 56% of the nitrogen leaves WWTP N°4 as N<sub>2</sub>. The emission of N<sub>2</sub> into the atmosphere does not generate entropy because of the high concentration of N<sub>2</sub> that is already present in the atmosphere (75% mass fraction). Similar considerations can be made for the other WWTPs. These examples demonstrate that the nitrogen performance of a WWTP can appear quite different if the different nitrogen compounds, their distribution in the individual mass flows and their dilution in the environment are considered. In this work, the eSEA



results were only compared to the nitrogen removal rate. For a more comprehensive analysis of the advantages and disadvantages of eSEA, it is advisable to also compare the results to those based on the LW and EQ indicators. The comparison of the use of eSEA and EQ to determine the nitrogen performance of WWT facilities is presented in Chapter 5.

#### 4.3.2 Determination of the best practice WWTP: energy-efficiency and cost-effectiveness

Nitrogen treatment requires expenses in the form of energy and costs. Energy is mostly used for aeration processes during nitrification. A certain concentration of dissolved oxygen ( $O_{2,diss.}$ ) is important in the nitrification process and, consequently, for long-term water quality. However, a very high concentration of  $O_{2,diss.}$  can lead to undesirable effects due to the incomplete denitrification caused by the recirculation of  $O_2$  from the aerobic to the anoxic reactor (Flores-Alsina et al. 2011). To compare WWTPs of different sizes, the values of both the energy-consumption and the costs were divided by the individual PE. The energy-efficiency was defined as the energy consumption that is required for every PE to achieve a reduction in statistical entropy. The cost-effectiveness was calculated as the  $\Delta H$  per PE-specific costs, which defines the cost-effectiveness of the nitrogen treatment as the reduction in the statistical entropy that is achieved for every EUR and PE. In Table 4-3 the nitrogen performance of the 5 analyzed Austrian WWTPs according to eSEA and the energy-efficiency and cost-effectiveness are presented. The best performances are indicated in bold.

**Table 4-3:** Comparison of the nitrogen performance of five Austrian WWTPs as assessed by eSEA, energy-efficiency and cost-effectiveness.

	WWTP N°1	WWTP N°2	WWTP N°3	WWTP N°4	WWTP N°5
<b><math>\Delta H</math></b> [%]	74	77	<b>83</b>	73	<b>85</b>
<b>Energy-efficiency</b> [kWh/PE/ $\Delta H$ %]	0.15	<b>0.11</b>	<b>0.12</b>	0.19	(a)
<b>Cost-effectiveness</b> [ $\Delta H$ %/€/PE]	<b>62</b>	(a)	23	32	8

(a) No data available

According to the eSEA results, WWTPs N°3 and N°5 exhibit the best nitrogen performance. However, WWTPs N°2 and N°3 exhibit the most energy-efficient nitrogen

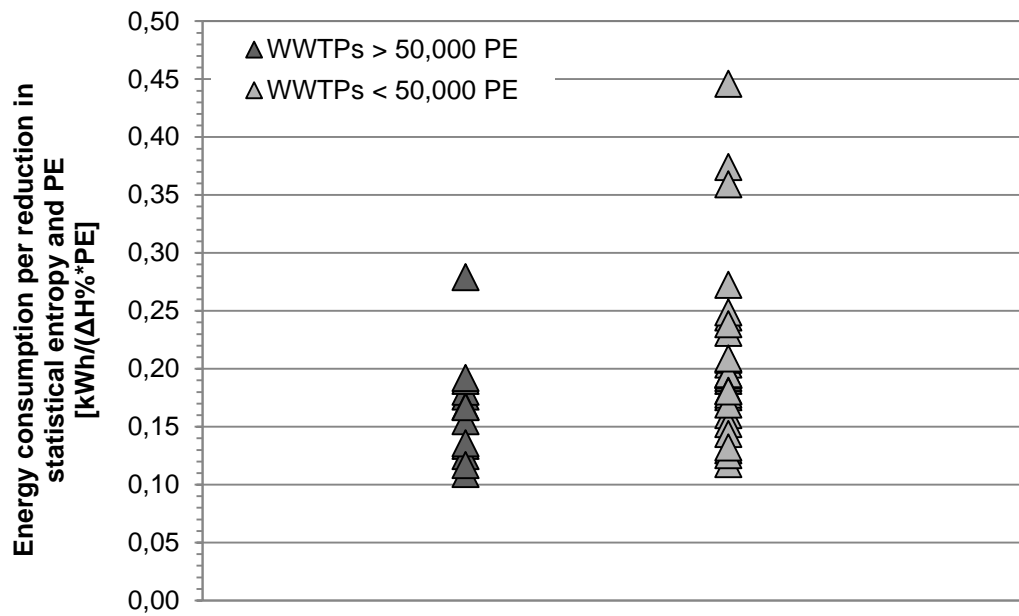
treatment, and WWTP N°1 achieves the highest cost-effectiveness. The results indicate that an energy-efficient nitrogen performance does not necessarily imply cost-effectiveness. However, a greater number of WWTPs needs to be investigated before this result can be generalized. Because all five WWTPs comply with Austrian mandatory emission standards, it is reasonable to nominate the most energy-efficient or the most cost-effective WWTP as the best practice WWTP, which in this case would be WWTP N°1, N°2 or N°3. A different approach would be to propose the best practice WWTP as the plant with good results in all 3 categories, which, according to the analysis presented in this work, would be WWTP N°3. In Austrian benchmarking, cost-effectiveness plays the decisive role, which is reasonable because the costs for energy consumption are included and the relationship between the energy consumption and the energy costs is usually proportional (Lindtner, et al., 2002), (Lindtner, 2009).

#### 4.3.3 The influence of plant size

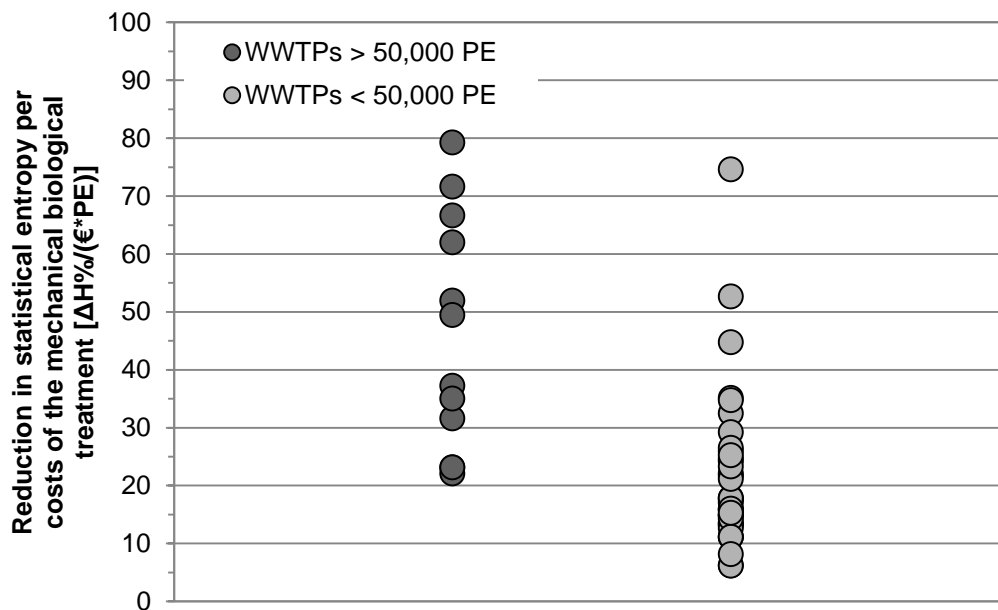
Large WWTPs tend to operate more energy-efficiently and cost-effective, according to the classical definition of both terms. In this work, both the energy-efficiency and cost-effectiveness are related to the nitrogen removal performance assessed by eSEA for 56 Austrian WWTPs. Table 4-4 gives an overview over the number of WWTPs among the different size groups. Figures 4.3 and 4.4 reveal the newly defined energy-efficiencies and cost-effectiveness of all the WWTPs.

**Table 4-4:** Overview over the number of WWTPs among the different size groups.

Size Group / PE									
10,000 - 20,000	20,000 - 30,000	30,000 - 40,000	40,000 - 50,000	50,000 - 60,000	60,000 - 70,000	70,000 - 80,000	80,000 - 90,000	90,000 - 100,000	>100,000
Number of WWTPs among the different size groups									
10	10	8	10	1	4	0	2	1	10
WWTPs < 50,000 PE				WWTPs > 50,000 PE					
Total number of small and large WWTPs									
38				18					



**Figure 4.3:** Energy-efficiency of 15 large WWTPs > 50,000 PE and 26 small WWTPs < 50,000 PE



**Figure 4.4:** Cost-effectiveness of 12 large WWTPs > 50,000 PE and 38 small WWTPs < 50,000 PE

Data of 38 small WWTPs (< 50,000 PE) and 18 large WWTPs (> 50,000 PE) are available. Among the small plants all size groups are equally represented while among

the large WWTPs those that are designed for more than 100,000 PE are overly represented.

The average energy-efficiency at  $0.16 \text{ kWh}/(\Delta H\% \cdot \text{PE})$  is higher for the large WWTPs ( $> 50,000 \text{ PE}$ ) than for the small plants ( $< 50,000 \text{ PE}$ ), at  $0.21 \text{ kWh}/(\Delta H\% \cdot \text{PE})$ . However, many small WWTPs can operate as energy-efficiently as larger plants (cf. Figure 4.3). For example, a WWTP, which serves 167,000 PE reports the same energy-efficient nitrogen removal performance ( $0.13 \text{ kWh}/(\text{PE} \cdot \Delta H)$ ) as a WWTP, which is responsible for 41,833 PE, and another WWTP, which serves only 22,000 PE. In total, 14 out of 15 large WWTPs and 16 out of 26 small WWTPs achieve energy-efficiency between 0.1 and  $0.2 \text{ kWh}/(\Delta H\% \cdot \text{PE})$  (numerical results are not shown in this chapter). These findings are not in accordance with the results of the state-of-the-art literature, which states that large WWTPs operate more energy-efficiently (Nowak, 2002), (Lindtner, et al., 2008), (Kroiss & Svardal, 2009), (Lindtner, 2010).

None of the smaller WWTPs reached the high cost-effectiveness of the largest WWTPs ( $79 \Delta H\%/(€ \cdot \text{PE})$ ) (cf. Figure 4.4). The average value for the large WWTPs ( $> 50,000 \text{ PE}$ ) is at  $46 \Delta H\%/(€ \cdot \text{PE})$  more than double the average value for the cost-effectiveness of the small plants ( $< 50,000 \text{ PE}$ ), at  $21 \Delta H\%/(€ \cdot \text{PE})$ . This result is in agreement with literature findings (Lindtner, et al., 2008), (Hernandez-Sancho & Sala-Garrido, 2009), (Lindtner, 2010). However, some WWTPs seem capable of achieving cost-effectiveness in the range of those of the large WWTPs. For example, 3 of the large WWTPs that serve 100,000 PE, 150,000 PE, and 200,000 PE, and 5 of the small WWTPs one responsible for 16,800 PE and four others designed between 40,000 and 48,000 PE report cost-effectiveness of approximately  $23 \Delta H\%/(€ \cdot \text{PE})$ . Another 3 large WWTPs designed for 70,000 PE, 180,000 PE, and 400,000 PE achieve cost-effectiveness in the range of 32 and  $37 \Delta H\%/(€ \cdot \text{PE})$ , comparable to the cost-effectiveness of several small WWTPs that serve between 39,000 and 45,000 PE. A WWTP designed for 167,000 PE also reports higher cost-effectiveness ( $79 \Delta H\%/(€ \cdot \text{PE})$ ) than a WWTP, which serves 950,000 PE ( $62 \Delta H\%/(€ \cdot \text{PE})$ ). Another WWTP constructed for only 35,000 PE achieves cost-effectiveness of  $75 \Delta H\%/(€ \cdot \text{PE})$ , a value in the range of the best cost-effectiveness among the large WWTPs ( $> 50,000 \text{ PE}$ ) (numerical results are not shown in this chapter). These results can be of particular importance for the design and operation of small, decentralized WWTPs.

## 4.4 Conclusions

The use of eSEA offers a more comprehensive assessment of the nitrogen performance of WWTPs than the nitrogen removal rate because it considers different nitrogen compounds, including gaseous emissions; the distribution of nitrogen in the wastewater, effluent, and sludge; and the dilution of the emissions in the environment. The application of eSEA rewards WWTPs that transform and transfer nitrogen compounds from the wastewater into harmless (or less harmful) species, such as  $\text{N}_2$  or  $\text{NO}_3^-$ , instead of into  $\text{NH}_4^+$  or  $\text{N}_{\text{org}}$ , which would be discharged into water bodies. The eSEA results can be related to the energy-consumption and costs of the nitrogen treatment. Thus, the evaluation can be extended to economic factors. The results of the analysis of 5 Austrian WWTPs demonstrate that an energy-efficient plant is not necessarily cost-effective. The nitrogen removal performances, the energy-efficiencies and cost-effectiveness of 56 different size WWTPs were compared, revealing that individual, small WWTPs (10,000-50,000 PE) are able to compete with the larger plants (50,000-950,000 PE). These results are interesting for the assessment of the advantages and disadvantages of small, decentralized WWTPs. It would be also interesting to determine to what extent the different nitrogen treatment processes influence the nitrogen removal performance according to eSEA and whether source separation (e.g., blackwater and graywater) has a positive impact on the nitrogen removal performance of WWTPs.

## 5 Implementation of Extended Statistical Entropy Analysis to the Effluent Quality Index of the Benchmarking Simulation Model N°2

### Abstract

Extended statistical entropy analysis (eSEA) is used to assess the nitrogen removal performance of wastewater treatment (WWT) as simulated by the Benchmarking Simulation Model No 2 (BSM N°2). For this purpose, six simulations are carried out that vary in the concentration of dissolved oxygen ( $O_{2,diss.}$ ) during the aerobic treatment. Three different types of wastewater, each with a different flow rate and pollution characteristic are employed.  $N_2O$  emissions as a result of the denitrification process are included in the model. The nitrogen removal performance is expressed as the reduction in statistical entropy  $\Delta H$  compared to the hypothetical reference situation of direct discharge of the wastewater into the river. The parameters chemical and biological oxygen demand (COD, BOD) and suspended solids (SS) are analogously expressed in terms of reduction of COD, BOD, and SS compared to a direct discharge of the wastewater to the river ( $\Delta EQ_{rest}$ ). Thus  $\Delta EQ_{rest}$  and  $\Delta H$  range between 0% and 100%.  $\Delta EQ_{new}$  is then defined as the weighted average of  $\Delta H$  and  $\Delta EQ_{rest}$ . The higher the value for  $\Delta EQ_{new}$  is the better is the entire cleaning performance of the particular WWT process. The results show that  $\Delta EQ_{new}$  is a more comprehensive indicator of the cleaning performance because in contrast to the traditional EQ it considers the characteristics of the wastewater, it includes all nitrogen compounds and their distribution in the different material flows such as the effluent, the off-gas, and the sludge. Furthermore, it is demonstrated that realistically expectable  $N_2O$  emissions have only a moderate impact on  $\Delta EQ_{new}$ .

### 5.1 Introduction

The Benchmarking Simulation Model No 2 (BSM N°2) models an activated sludge large-scale wastewater treatment plant (WWTP) at the level of the whole plant aiming at a more stable and improved effluent quality. The BSM N°2 considers both pretreatment of the wastewater and sludge treatment thus including seasonal effects on the WWTP in terms of temperature variations and changing influent flow rate patterns (Jeppsson, et al., 2007). The effluent quality is measured by the Effluent Quality Index (EQ), which considers the loads of SS, COD, BOD, TKN, and  $NO_3^-$ . Every parameter is attached with an individual weighting factor to reflect the particular ecological harming potential. In the BSM N°2  $N_{org}$

is differentiated as soluble biodegradable  $N_{org}$  (SBN) and particulate biodegradable  $N_{org}$  (PBN). However, the EQ does not differentiate between  $NH_4^+$ , SBN and PBN. Furthermore, gaseous losses such as  $N_2O$  are disregarded. Yet,  $N_2O$  emissions caused by WWT are important due to the great greenhouse gas (GHG) potential of  $N_2O$ , which is 296 times bigger than the potential of  $CO_2$ , and because wastewater is worldwide the sixth largest contributor to  $N_2O$  emissions (Ehhalt & Prather, 2001), (Gupta & Singh, 2012). It was found that the  $O_2$  concentration in the aeration tanks is one of the main operational parameters influencing the production of  $N_2O$  (Kampschreur, et al., 2009), (Lolito, et al., 2012). At  $O_2$  concentrations of 1  $mgO_2/L$   $N_2O$  emissions increase due to incomplete nitrification compared to the default open-loop control strategy.  $O_2$  concentrations below 1 $mg/L$  can cause  $N_2O$  emissions that correspond to 10% of the initial nitrogen load (Goreau, et al., 1980). Other studies confirm that low  $O_2$  concentrations lead to increased  $N_2O$  emissions (Dumit, et al., 2011), (Hu, et al., 2011), (Aboobakar, et al., 2012), (Winter, et al., 2012), (Jia, et al., 2013). On the other hand,  $O_2$  concentrations of 3  $mgO_2/L$  also lead to increased  $N_2O$  emissions due to incomplete denitrification caused by recirculation of the  $O_2$  from the aerobic to the anoxic reactor (Flores-Alsina, et al., 2011). The estimation of GHG emissions related to WWT processes has been solved through different modeling approaches (Snip, 2010), (Rodriguez-Garcia, et al., 2012), (Corominas, et al., 2012). Snip and colleagues model  $N_2O$  emissions within the BSM N°2 disregarding the potential emissions from the aerobic process. They, in turn, find that a change in the  $NH_4^+$  concentration has the highest effect on the  $N_2O$  production whereas the  $O_2$  concentration has almost no influence (Snip, 2010). The degree of accumulated  $NH_4^+$  at the end of the anoxic phase effectively enhances the  $N_2O$  production (Yu, et al., 2010), (Dumit, et al., 2011), (Wunderlin, et al., 2013). Based on the BSM N°2 it is also shown that in addition to the  $O_2$  concentration, the control of the internal recycle flow and the SS significantly influence the  $N_2O$  emissions (Flores-Alsina, et al., 2011). Furthermore, other parameters like temperature, pH, and even the copper concentration in the wastewater are found to have a considerable effect on the  $N_2O$  production (Hu, et al., 2011), (Zhang, et al., 2012), (Corominas, et al., 2012), (Law, et al., 2011), (Zhu, et al., 2013). Recent findings show a seasonal dynamic of  $N_2O$  emissions, which is not yet fully understood (Daelman, et al., in press.). A comprehensive review of literature published in 2011 on parameters affecting  $N_2O$  emissions from WWT facilities is presented in (Shaw & Ko, 2012). However,  $N_2O$  emissions are not yet considered in the assessment of the N-removal performance and the overall cleaning performance.

Apart from its importance for the  $\text{N}_2\text{O}$  production the dissolved  $\text{O}_2$  has been determined as one of the most important process variables influencing the entire nitrification and denitrification process, thus affecting the nitrogen removal performance of the WWT (Hiatt & Grady Jr, 2008). Based on studies performed using the BSM N°2 it was derived that the process control that regulates the  $\text{O}_2$  concentration in two aeration tanks each to  $2 \text{ gO}_2/\text{m}^3$  and  $1 \text{ gO}_2/\text{m}^3$  yields a lower total nitrogen and a lower  $\text{NO}_3^-$  load in the effluent compared to an operating condition where the dissolved  $\text{O}_2$  concentration is set to  $2 \text{ gO}_2/\text{m}^3$  in one aeration tank. Dynamic  $\text{O}_2$  dosage has the advantage that the  $\text{O}_2$  input can be minimized. It results in a lower total nitrogen and  $\text{NO}_3^-$  load but in turn, yields an increased  $\text{NH}_4^+$  load in the effluent (Nopens, et al., 2010). In their work, Vanrolleghem and Gillot conclude that the dissolved  $\text{O}_2$  concentration should be controlled in every aeration tank because the performance, measured by the EQ improves significantly compared to the open-loop strategy (Vanrolleghem & Gillot, 2002). Haemelick and colleagues evaluate different dissolved  $\text{O}_2$  operating conditions and identify the best option in which dissolved  $\text{O}_2$  is controlled in all aeration tanks with optimal concentrations of  $1 \text{ gO}_2/\text{m}^3$  each (Haemelick, 2000). Yuan and colleagues simulate the treatment of synthetic domestic wastewater in a step-feed anaerobic-multiple anoxic/oxic-membrane bioreactor and find that a dissolved  $\text{O}_2$  concentration between  $0.8$  and  $1.2 \text{ mgO}_2/\text{L}$  is optimal for a high total nitrogen removal rate (Yuan, et al., 2012). In addition to process parameters like the  $\text{O}_2$  concentration the composition of the wastewater itself can also influence the cleaning performance. Low pollution loads of the wastewater due to mixing with rainwater, for example, can cause incomplete denitrification and can therefore worsen the nitrogen performance (Coen, et al., 1996), (Kessler, 2011).

In the previous chapter it has been demonstrated that eSEA is suitable for evaluating the nitrogen removal performance of WWTPs and that eSEA provides a more comprehensive assessment of the nitrogen removal performance than the nitrogen removal rate because, unlike the nitrogen removal rate, it considers the distribution of all nitrogen compounds in the different material flows such as the effluent, the sludge, and the off-gas.

The purpose of this chapter therefore is to improve the assessment of the nitrogen removal performance in the BSM N°2 by implementing eSEA to the traditional EQ.



## 5.2 Methods and Materials

### 5.2.1 The simulation of WWT according to the BSM N°2 setup including the modeling of greenhouse gas (GHG) emissions

Different WWT simulations are carried out based on the BSM N°2 setup including the simulation of GHG emissions according to the model developed by Snip and colleagues (Jeppsson, et al., 2007), (Snip, 2010). The BSM N°2 is operated with preceding denitrification. The anoxic tank volumes are 1,500 m<sup>3</sup> each and the aerated tank volumes are 3,000 m<sup>3</sup> each.

Three different wastewater types are used: the wastewater type I is the official dynamic influent file of the BSM N°2 and the wastewater types II and III are constructed influent files based on real data of WWTPs. The wastewater type III represents a quite diluted wastewater compared to the other wastewater types. The parameters characterizing the wastewater types and volumes that are relevant for the traditional EQ and eSEA are displayed in Table 5-1.

**Table 5-1:** Annual average influent data

Influent, Wastewater type	WW inflow	BOD	COD	SS	NH <sub>4</sub> <sup>+</sup>	SBN	PBN	Total N-load
		Concentration in the wastewater						
	<i>m<sup>3</sup>/day</i>	<i>g/m<sup>3</sup></i>			<i>gN/m<sup>3</sup></i>			<i>kg N/day</i>
I	861	301	587	54.7	26.8	6.4	18.5	44.5
II	864	274	524	151	35.3	2.52	2.52	34.9
III	528	110	213	21.3	15.3	1.31	3.40	10.6

Table 5-1 reveals that the wastewater types I and II have a similar flow rate. The wastewater type I shows a higher pollution load regarding total nitrogen but a different distribution of NH<sub>4</sub><sup>+</sup>, SBN, and PBN in the wastewater. Both the BOD and COD loads are slightly higher for the wastewater type I compared to the wastewater type II. The wastewater type II, in turn, has almost a 3-fold higher SS-load compared to the wastewater type I. The wastewater type III represents a much diluted wastewater compared to the other wastewater types and has also a low flow rate.

The only operational parameter that is varied during the simulations is the O<sub>2</sub> concentration in the three aeration tanks. The O<sub>2</sub> concentration is varied because in

this chapter, we aim at obtaining significantly different nitrogen removal performances to demonstrate the benefits of using eSEA for evaluation of the nitrogen removal performance over the traditional EQ. Literature findings show that the  $O_2$  concentration has a major influence on both the nitrification and denitrification. Table 5-2 summarizes the conditions of the realized simulations including the wastewater type used and the  $O_2$  concentration in the three aeration tanks.

**Table 5-2:** Summary of the performed WWT simulations

Simulation #	Influent, Wastewater type	Aeration tank		
		1	2	3
		mgO <sub>2</sub> /L		
1	I	1	1	1
2		2	2	2
3	II	1	1	1
4		2	2	2
5	III	1	1	1
6		2	2	2

Table 5-2 shows that the  $O_2$  concentration in the aeration tanks is controlled and varied from 1 mgO<sub>2</sub>/L to 2 mgO<sub>2</sub>/L. This range has been chosen because former work has revealed that  $O_2$  concentrations below 1 mgO<sub>2</sub>/L and above 3 mgO<sub>2</sub>/L yield overall undesirable results. Sludge age is an important parameter, in particular for the nitrification process. For the Simulations #1, #2, #3, and #4 the sludge age is 16 days and for the Simulations #6 and #7 sludge age extends to 20 days. Hence, the sludge age in these simulations is more beneficial for the nitrification process compared to the other simulations.

Within the BSM N°2 not all sorts of data are assessed that are necessary for eSEA. Therefore the amount of  $N_2$  due to denitrification is calculated based on the amount of the reacted  $NO_3^-$  in the anoxic tanks. For simplicity, it is assumed that all  $N-NO_3^-$  in the last anoxic tank minus the amount of  $N-N_2O$  is converted to  $N_2$  through the denitrification process. The nitrogen concentration in the sludge is finally calculated from the mass balance (nitrogen input minus nitrogen in the effluent minus nitrogen in the off-gas).

Recent findings indicate that the aerobic nitrification process might be an even more dominant source for N<sub>2</sub>O production than the denitrification (Ahn, et al., 2010), (Yu, et al., 2010). However, the emissions that can occur during the aerobic processes are not covered by the model used in this work and therefore, the measured amounts of N<sub>2</sub>O are likely underestimated (Snip, 2010).

### 5.2.2 Effluent Quality Index (EQ) used in BSM N°2

The EQ describes the effluent quality by means of the indicators SS, COD, BOD, TKN and NO<sub>3</sub><sup>-</sup> in the effluent in units of kg pollution (PU) per day.

$$EQ = \frac{1}{(t_2 - t_1) * 1000} \int_{t_1}^{t_2} [B_{SS} * SS_e(t) + B_{COD} * COD_e(t) + B_{TKN} * S_{TKN,e}(t) + B_{NO} * S_{NO,e}(t) + B_{BOD5} * BOD_{5,e}(t)] * Q_e(t) dt$$

(Eq.5.1)

(t<sub>2</sub>-t<sub>1</sub>): total evaluation period; SS: Suspended solids in gSS/m<sup>3</sup>; TKN (SBN+PBN+NH<sub>4</sub><sup>+</sup>) in gN/m<sup>3</sup>; NO (NO<sub>3</sub><sup>-</sup>) in gN/m<sup>3</sup>; BOD<sub>5</sub>: Biological O<sub>2</sub> demand in 5 days in gBOD/m<sup>3</sup>; Q<sub>e</sub>: Effluent in m<sup>3</sup>/day

B: dimensionless weighting factors; initially: B<sub>SS</sub>=2; B<sub>COD</sub>=1; B<sub>TKN</sub>=20; B<sub>NO</sub>=20; B<sub>BOD5</sub>=2 (Vanrolleghem et al. 1996); in further work the weighting factors have been modified to: B<sub>SS</sub>=2; B<sub>COD</sub>=1; B<sub>TKN</sub>=30; B<sub>NOx</sub>=10; B<sub>BOD5</sub>=2 (Nopens, et al., 2010).

Originally, the same weighting factors were assigned to both TKN and nitrate, which lead to the problem that a process control that achieves low concentrations of TKN in the effluent would not be rewarded. However, from an ecological point of view, low concentrations of NH<sub>4</sub><sup>+</sup> and N<sub>org</sub> in the effluent are clearly preferential and therefore the weighting factors have been finally adapted (Jeppsson, et al., 2007), (Nopens, et al., 2010).

COD stands for all organic, particulate and soluble oxidable chemical compounds that might be more or less persistent in water while BOD reflects the amount of organic compounds that will be broken down by organisms. Such compounds are however not further specified. SS can be especially dangerous to water bodies because they can carry pathogens on their surface. The particle size is hereby important because the total surface area per unit mass of particle increases with smaller particle size, and then the pollutant load can also increase. Although the COD, BOD, and SS are mostly removed from the wastewater, some amount of organic compounds and SS will still be

discharged and eventually the low weighting factors will not reflect the toxicological potential appropriately (Tyagi, et al., 2007). The nitrogen removal performance within the EQ is defined through the loads of both TKN and  $\text{NO}_3^-$  in the effluent. The latest weighting factors imply TKN to be 3 times more relevant to the receiving waters than  $\text{NO}_3^-$ , which is confirmed by the impact factors for aquatic eutrophication in various Life Cycle Impact Assessment methods (Heijungs R., 1992), (Goedkoop & Spriensma, 2001), (Guinée, et al., 2002), (Pennington, et al., 2005), (Pennington, et al., 2006). However the traditional EQ neither considers the difference of the environmental relevance between  $\text{NH}_4^+$ , SBN, and PBN nor the impact of  $\text{N}_2\text{O}$  on the atmosphere. The distribution of the nitrogen in the sludge is also excluded. The initial pollution load of the wastewater does not play any role either. Consequently, the cleaning performance of the WWT cannot be fully recompensed by the traditional EQ. A WWT system that, for example, emits less  $\text{N}_2\text{O}$  to the atmosphere would not be rewarded by the traditional EQ compared to a WWT that generates high emissions of  $\text{N}_2\text{O}$ . Therefore, in Section 5.3.1, the traditional EQ is redefined.

## 5.3 Results and discussion

### 5.3.1 The implementation of eSEA as to the EQ

In this section, eSEA is implemented into the traditional EQ leading to a redefinition of the EQ. In the first step the traditional EQ is broken down into the nitrogen part and the remaining indicators of the effluent quality (Equations 5.2-5.4).

$$\text{EQ} = \text{EQ}_N + \text{EQ}_{\text{rest}} \quad (\text{Eq. 5.2})$$

where

$$\text{EQ}_N = \text{EQ}_{\text{TKN}} + \text{EQ}_{\text{NO}} \quad (\text{Eq. 5.3})$$

and

$$\text{EQ}_{\text{rest}} = \text{EQ}_{\text{SS}} + \text{EQ}_{\text{COD}} + \text{EQ}_{\text{BOD5}} \quad (\text{Eq. 5.4})$$

Next  $\text{EQ}_N$  is substituted by  $\Delta H$  and  $\text{EQ}_{\text{rest}}$  is analogously redefined as the reduction of  $\text{EQ}_{\text{rest}}$  compared to the direct discharge of the wastewater and thus the COD,  $\text{BOD}_5$ , and SS load to the receiving waters (Equations 5.5 and 5.6).

$$\Delta H_N = \frac{H_{\text{N,noWWT}} - H_{\text{N,afterWWT}}}{H_{\text{N,noWWT}}} * 100 \quad (\text{Eq. 5.5})$$

and

$$\Delta EQ_{rest} = \frac{EQ_{rest,noWWT} - EQ_{rest,afterWWT}}{EQ_{rest,noWWT}} * 100 \quad (\text{Eq. 5.6})$$

$\Delta EQ_{new}$  is then defined as the weighted average of  $\Delta H$  and  $\Delta EQ_{rest}$  according to Equation 5.7. The weighting factor for  $\Delta H$  is based on the weighting factors as they are currently used in the BSM N°2 (Equation 5.1 in Section 5.2.2). However, it is questionable whether the weighting factor applied to  $\Delta H$  adequately represents the GHG potential of  $N_2O$  compared to the potential impact of the other parameters such as the aquatic N-compounds, COD,  $BOD_5$ , and SS.

$$\Delta EQ_{new} = \frac{12 * \Delta H_N + \Delta EQ_{rest}}{13} \quad (\text{Eq. 5.7})$$

$\Delta EQ_{new}$  is now expressed in % and ranges from 0% and 100%. The higher the value for  $EQ_{new}$  the better is the entire cleaning performance of the WWT including  $N_2O$  emissions.

### 5.3.2 Comparison of the traditional EQ and the new defined EQ

The cleaning performance of the realized WWT simulations is evaluated according to the traditional EQ (here:  $EQ_{OUT}$ ), the EQ removal rate ( $\Delta EQ$ , calculated from the reduction from  $EQ_{IN}$  to  $EQ_{OUT}$ , where  $EQ_{IN}$  is the EQ from the untreated wastewater), the classical nitrogen removal rate ( $\Delta N$ , the difference between the total nitrogen in the wastewater compared to the effluent), and the newly defined indicator,  $\Delta EQ_{new}$ .  $\Delta EQ$  is additionally divided and presented for N ( $\Delta EQ_N$ ) and COD, BOD, and SS ( $\Delta EQ_{rest}$ ). The WWT simulations vary in the type and the amount of the wastewater and the alteration of the  $O_2$  concentration during the aerobic part of the biological treatment between 1 mg/L and 2 mg/L. Simulations #1, #3, and #5 are performed with 1  $mgO_2/L$  while simulations #2, #4, and #6 are carried out at a concentration of 2  $mgO_2/L$  (cf. Table 2, Section 2.1). Table 3 summarizes the simulated  $N_2O$  emissions, the results for  $EQ_{IN}$ ,  $EQ_{OUT}$ ,  $\Delta EQ$ ,  $\Delta EQ_{rest}$ ,  $\Delta EQ_N$ ,  $\Delta N$ ,  $\Delta H$ , and  $\Delta EQ_{new}$  for the usual evaluation period of one year.

**Table 5-3:** N<sub>2</sub>O emissions, traditional EQ of the wastewater (EQ<sub>IN</sub>) and the effluent (EQ<sub>OUT</sub>), EQ removal rate ( $\Delta EQ$ ), EQ removal rate for COD, BOD, and SS ( $\Delta EQ_{rest}$ ), EQ removal rate for nitrogen ( $\Delta EQ_N$ ), nitrogen removal rate ( $\Delta N$ ), nitrogen removal performance according to eSEA ( $\Delta H$ ), and the EQ<sub>new</sub> for all WWT simulations

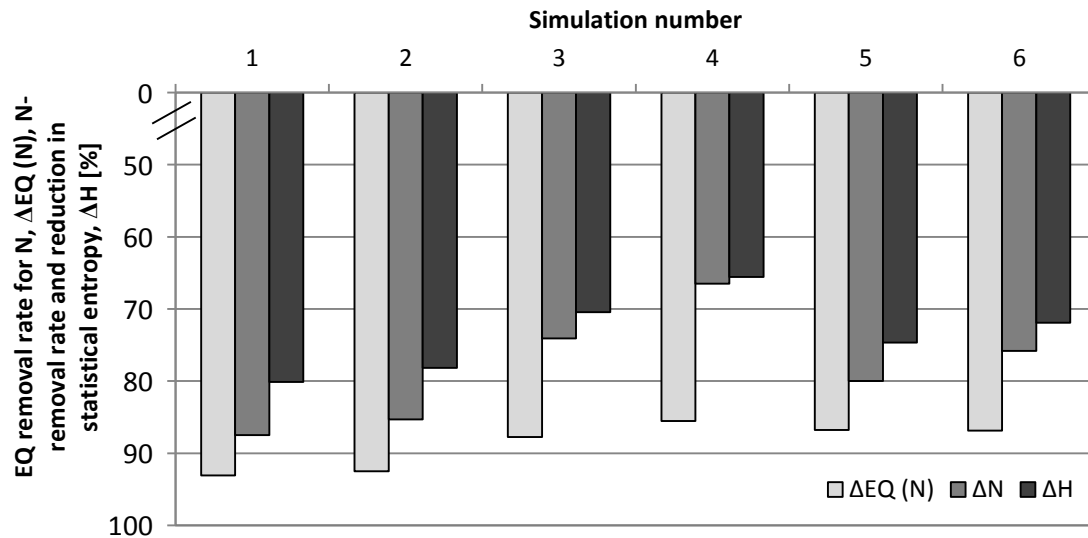
Simulation #	N <sub>2</sub> O		EQ <sub>IN</sub>	EQ <sub>OUT</sub>	$\Delta EQ$	$\Delta EQ_{rest}$	$\Delta EQ_N$	$\Delta N$	$\Delta H$	$\Delta EQ_{new}$
	kgN-N <sub>2</sub> O/day	%N <sub>IN</sub>	kgPU/day	kgPU/day	%	%	%	%	%	%
1	3.3	0.35	58878	4203	93	93	93	88	81	82
2	3.2	0.34		4379	93	93	93	85	79	80
3	3.7	0.44	53571	4682	91	94	88	74	71	73
4	3.4	0.41		5230	90	94	86	67	66	68
5	0.98	0.39	13630	1640	88	89	87	80	75	76
6	0.94	0.37		1629	88	90	87	76	72	73

Table 5-3 reveals that the pollution load in the effluent, indicated by EQ<sub>OUT</sub> varies significantly from 1,629 kgPU/day to 5,230 kgPU/day. However, the EQ removal rates ( $\Delta EQ$ ) are less different ranging from 88% to 93%. The EQ removal rates for nitrogen ( $\Delta EQ_N$ ) are calculated between 86% and 93% and those for COD, BOD, and SS ( $\Delta EQ_{rest}$ ) differ between 89% and 94%. The N-removal rates ( $\Delta N$ ) vary between 67% and 88%.  $\Delta H$  values are obtained between 66 % and 81 %. These results are in accordance with the findings for Austrian WWTPs (Sobańtka and Rechberger 2013). The simulated N<sub>2</sub>O emissions are found in the lower range (0.35 % – 0.44 % relative to the nitrogen feed in the wastewater; cf. Table 5-3) among literature values (Kampschreur et al. 2006).  $\Delta EQ_{new}$  ranges between 68% and 82%.

Table 5-3 also shows that EQ<sub>OUT</sub>,  $\Delta N$ ,  $\Delta H$ , and  $\Delta EQ_{new}$  assess the simulations that were performed with 1 mgO<sub>2</sub>/L as advantageous compared to those that were carried out with 2mgO<sub>2</sub>/L (lower EQ<sub>OUT</sub>, higher  $\Delta N$ , higher  $\Delta H$ , and higher  $\Delta EQ_{new}$ ). Lower traditional EQ values at an O<sub>2</sub> concentration of 1 mgO<sub>2</sub>/L are in accordance with literature findings (Haemelick et al. 2000, Nopens et al. 2010, Yuan et al. 2012). This effect is however not reflected by  $\Delta EQ_N$  or  $\Delta EQ$ . N<sub>2</sub>O emissions are slightly lower at an

O<sub>2</sub> set point of 2 mgO<sub>2</sub>/L than at 1 mg O<sub>2</sub>/L. This also validates the findings in literature (Kampschreur et al. 2009, Snip et al. 2010, Flores-Alsina et al. 2011). The faintly altered N<sub>2</sub>O emissions however hardly affect the overall nitrogen removal performance measured by  $\Delta H$ , which puts the relevance of N<sub>2</sub>O for the overall nitrogen removal performance somehow in perspective. A more detailed investigation of the influence of N<sub>2</sub>O for the overall nitrogen removal performance according to eSEA is additionally discussed in Section 3.3. Note that the simulation of N<sub>2</sub>O emissions as performed in this work only considers the N<sub>2</sub>O from the denitrification process, disregarding the emissions from the nitrification process. Thus, the N<sub>2</sub>O emissions are likely underestimated.

The aim of this paper is to improve evaluation of the nitrogen removal performance within the BSM N°2 by implementing eSEA into the traditional EQ. Therefore, in Figure 5-1, the entropy based indicator is discussed in comparison to the nitrogen removal performance according to the EQ removal rate for nitrogen,  $\Delta EQ_N$ , and the classical nitrogen removal rate,  $\Delta N$ .



**Figure 5.1:** EQ removal rate for nitrogen ( $\Delta EQ_N$ ), nitrogen removal rate ( $\Delta N$ ), and the nitrogen removal performance according to eSEA ( $\Delta H$ ) for all WWT simulations

Figure 5-1 shows that the Simulations #1, #3, and #5, which are performed with an O<sub>2</sub> concentration of 1 mgO<sub>2</sub>/L show higher nitrogen removal rates and higher  $\Delta H$  values compared to the Simulations #2, #4, and #6, which are carried out at a concentration of 2 mgO<sub>2</sub>/L.  $\Delta EQ_N$  in turn, does not show this trend:  $\Delta EQ_N$  is the same for the

Simulations #1 and #2 (93%) as well as for the Simulations #5 and #6 (87%). It is slightly higher for the Simulation #3 (88%) compared to the value for the Simulation #4 (86%). To understand the differences in the nitrogen removal performance between  $\Delta EQ_N$ ,  $\Delta N$ , and  $\Delta H$  we must on one hand consider the nitrogen loads in the wastewater and the effluent and on the other hand the distribution of the particular nitrogen compounds in the wastewater, the effluent, the off-gas, and the sludge.  $N_2$  in the off-gas does not contribute to statistical entropy because it is received by the atmosphere with a natural  $N_2$  background concentration of approximately 75%. The differences between  $N_2O$  emissions of different simulations are small compared to the other nitrogen emissions and therefore have only a small contribution to statistical entropy (cf. Table 5-3). The extent of statistical entropy produced due to the transfer of  $N_{org}$  to the sludge is comparable for all 6 simulations (not shown here numerically). Hence, the differences in the effluent are the main responsible factors affecting the nitrogen removal performance assessed by eSEA. The concentrations and loads of the nitrogen compounds in the different wastewater types can be found in Table 5-1 in Chapter 5.2.1. The loads of the relevant nitrogen compounds in the effluent are shown in Table 5-4.

**Table 5-4:** Loads of the different nitrogen compounds in the effluent for all simulations performed

	Simulation #					
	1	2	3	4	5	6
	Load					
	kgN/day					
N- $NO_3^-$	3.7	4.8	7.2	10	1.1	1.8
N- $NH_4^+$	0.17	8.7 E-2	0.31	0.16	0.45	0.21
SBN	1.7	1.6	1.6	1.5	0.59	0.58
PBN	2.6 E-2	2.6 E-2	2.6 E-2	2.6 E-2	5.3 E-3	4.7 E-3
TKN	1.9	1.8	1.7	1.9	1.1	0.8

Table 5-4 demonstrates that the loads of SBN and PBN are not affected by a change of the  $O_2$  concentration from 1  $mgO_2/L$  to 2  $mgO_2/L$ . The main differences are found between the loads of N- $NO_3^-$  and N- $NH_4^+$ . The Simulations #1, #3, and #5 lead to a lower N- $NO_3^-$  and to a higher N- $NH_4^+$  load in the effluent compared to the Simulations #2, #4, and #6. This result is comprehensible because the nitrification process that



converts  $\text{NH}_4^+$  to  $\text{NO}_3^-$  depends upon presence of  $\text{O}_2$  and the denitrification process depends on absence of soluble  $\text{O}_2$ . Less  $\text{O}_2$  available thus means a discrimination of nitrification against denitrification and finally more  $\text{NH}_4^+$  and less  $\text{NO}_3^-$ . The  $\Delta\text{EQ}_\text{N}$  values are almost identical for the Simulations #3 to #6 although the  $\Delta\text{N}$  and the  $\Delta\text{H}$  values as well as the emission loads of  $\text{NO}_3^-$  and  $\text{NH}_4^+$  in the effluent differ considerably (cf. Table 5-3 and Figure 5-1). The only methodical difference between the indicators nitrogen removal rate,  $\Delta\text{N}$ , and the EQ removal rate for nitrogen,  $\Delta\text{EQ}_\text{N}$ , is that  $\Delta\text{EQ}_\text{N}$  differentiates between TKN and  $\text{NO}_3^-$  by applying different weighting factors (cf. Equation 1 in Chapter 5.2.2). The weighting factors for COD,  $\text{BOD}_5$ , SS, and nitrogen were initially derived based on discharge permits for Denmark and Flanders (Vanrolleghem et al. 1996). However TKN and  $\text{NO}_3^-$  had the same weighting factor ( $B_{\text{TKN}}=B_{\text{NO}_3^-}=20$ , cf. Equation 1 in Chapter 5.2.2) and were later adapted to  $B_{\text{TKN}}=30$  and  $B_{\text{NO}_3^-}=10$  for better agreement with ecological aspects (Nopens et al. 2010). The weighting factors are thus based on experts' assessment of the harming potential of TKN and  $\text{NO}_3^-$  and can be questioned.

In eSEA all nitrogen compounds are differentiated based on the corresponding natural background concentrations of the particular nitrogen compounds in the unstressed environment (Sobańka et al. 2012, Sobańka and Rechberger 2013). The eSEA distinguishes the nitrogen compounds based on a naturally existing relationship and thus offers a reasonable alternative to the weighting factors in the EQ. The concentrations of the particular nitrogen compounds in the effluent and the corresponding natural background concentrations are displayed in Table 5-5.

**Table 5-5:** Concentrations of the different nitrogen compounds in the effluent for all simulations performed and the naturally occurring background concentrations of the particular nitrogen compounds in rivers

	Simulation #						Natural background concentration
	1	2	3	4	5	6	
	Concentration						
	gN/m³						
N-NO <sub>3</sub> <sup>-</sup>	4.3	5.6	8.3	12	2.0	3.4	1.0 - 4.0 <sup>(1)</sup>
N-NH <sub>4</sub> <sup>+</sup>	0.20	0.10	0.36	0.18	0.85	0.40	0.01 – 0.05 <sup>(2)</sup>
SBN	1.9	1.89	1.8	1.8	1.1	1.1	0.1 – 0.4 <sup>(2)</sup>
PBN	3.0 E-2	3.0 E-2	3.0 E-2	3.0 E-2	1 E-2	1 E-2	0.1 – 0.4 <sup>(2)</sup>
TKN	2.2	2.0	2.2	2.0	2.0	1.5	

<sup>(1)</sup> Values based on (BGBI II Nr, 99/2010) <sup>(2)</sup> approximated

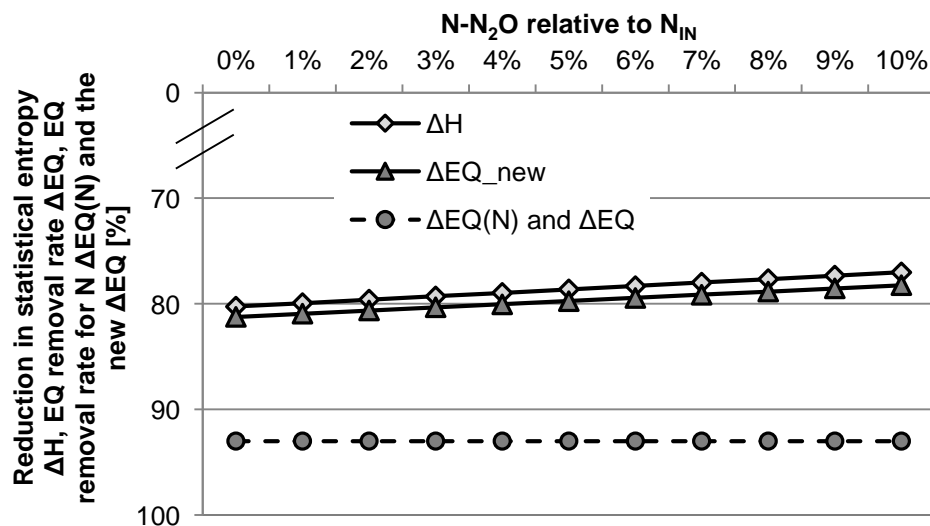
Table 5-5 shows a range of naturally occurring background concentrations for  $\text{NO}_3^-$ ,  $\text{NH}_4^+$ , SBN, and PBN. According to the Austrian Water Act rivers of very good and good water quality can contain  $\text{NO}_3^-$  between 1 mgN/L and 4 mgN/L (BGBl II Nr, 99/2010). Furthermore, according to the Austrian Water Act a dissolved organic carbon (DOC) concentration of 1 mg/L to 4 mg/L represents rivers with a very good and good water quality depending on the hydro-geological conditions. Assuming a carbon-nitrogen ratio of 10 to 1, SBN concentrations between 0.1 mgN/L to 0.4 mgN/L can be expected. PBN concentrations are likely to be found in the same range as for SBN since particulate organic matter is always present in rivers. The  $\text{NH}_4^+$  background concentration is set between 0.01 mgN/L to 0.05 mgN/L, which is considered as reasonable. For calculation of eSEA in this work the lower values of the background concentrations presented in Table 5-5 are used. Note that the  $\Delta H$  values would increase if the upper values for the background concentrations were used because  $H_{\text{afterWWT}}$  would decrease due to a shrinking difference between the emission concentrations and the background concentrations (cf. Figure 4.1). However, for the simulations presented in this work the  $\Delta H$  values would change only marginally (not shown here numerically) as the ranges for the background concentrations are rather narrow.

Generally, N- $\text{NH}_4^+$  has a higher environmental impact on water bodies than the same amount of N- $\text{NO}_3^-$  (Heijungs, et al., 1992), (Guinée, et al., 2002). Discharge of a certain amount of N- $\text{NH}_4^+$  would in fact generate more entropy than the same amount of N- $\text{NO}_3^-$  because the natural background concentration of N- $\text{NH}_4^+$  is approximately 2 orders of magnitude lower than that of N- $\text{NO}_3^-$  (cf. Table 5-5). However, the emission of, for example, double the  $\text{NH}_4^+$  concentration will not generate double the entropy because for calculation of eSEA logarithmic functions are used (Sobantka, et al., 2012). Such logarithmic trend can also be found for determination of ecotoxicological effects (Berenzen, et al., 2001), (Camargo, et al., 2005), (Carpenter & Lathrop, 2008), (Hamlin, 2006), (Hannas, et al., 2010), (Hickey & Martin, 2009), (De Koekkoek, 2005). In the simulations presented in this work the N- $\text{NO}_3^-$  concentrations are significantly higher than those for N- $\text{NH}_4^+$  (cf. Table 5-5). The higher  $\text{NO}_3^-$  emissions in the Simulations #2, #4, and #6 therefore generate more entropy than the elevated  $\text{NH}_4^+$  emissions in the Simulations #1, #3, and #5 leading to lower  $H_{\text{afterWWT}}$  values and higher  $\Delta H$  values for the Simulations #1, #3, and #5.

Note that the wastewater and effluent flow rates and the concentrations of COD, BOD<sub>5</sub>, SS, and the individual nitrogen compounds vary over the entire evaluation period of one year. For example, for Simulation #1 the average value for NO<sub>3</sub><sup>-</sup> within the entire evaluation period is 7.59 gN/m<sup>3</sup> ± 23% but it can vary ±100% for NH<sub>4</sub><sup>+</sup>, for instance. Because in this work we use the average values of the entire evaluation period the fluctuations of the cleaning performance are not addressed. Principally, the calculation of eSEA could be implemented into the BSM N°2 and computed for every time step. That way, the variation in the cleaning performance could be displayed for the entire evaluation period.

### 5.3.3 Scenario analysis: relevance of N<sub>2</sub>O for the overall nitrogen performance

In this section the influence of N<sub>2</sub>O emissions to the overall performance of the WWT is investigated in more detail. For this purpose the N<sub>2</sub>O emissions of simulation #1 are varied between 0 % of the nitrogen in the wastewater (N<sub>IN</sub>) and 10 % N<sub>IN</sub> (3.95 kgN-N<sub>2</sub>O/day). This covers a wide range of realistically expectable N<sub>2</sub>O emissions (Kampschreur, et al., 2009). Figure 5-2 shows how the N<sub>2</sub>O emissions influence  $\Delta H$  and in consequence  $\Delta EQ_{new}$ . Note that neither  $\Delta EQ_N$  nor the traditional EQ would be affected by a variation of N<sub>2</sub>O emissions at all because they only consider the compounds in the effluent.



**Figure 5.2:** Effect of N<sub>2</sub>O-emissions on the nitrogen removal performance measured by  $\Delta EQ_N$  and  $\Delta H$  and on the entire cleaning performance according to both  $\Delta EQ$  and  $\Delta EQ_{new}$

Figure 5.2 shows that both  $\Delta H$  and  $\Delta EQ_{new}$  decrease with increasing  $N_2O$  emissions (deterioration of both the nitrogen removal performance and the entire cleaning performance).  $\Delta EQ_{new}$  reacts less strongly (marginally smaller slope) to a change of the  $N_2O$  emissions compared to  $\Delta H$  (cf. Figure 5.2) because it also considers the parameters COD, BOD, and SS and these are not affected by an alteration of  $N_2O$  emissions. Figure 5.2 also reveals that the contribution of  $N_2O$  emissions to the overall N-removal performance is rather low:  $\Delta H$  ranges between 80 % for 0 % N- $N_2O$  relative to  $N_{IN}$  and 77 % for 10 % N- $N_2O$  relative to  $N_{IN}$  and  $\Delta EQ_{new}$  ranges between 81 % for 0 % N- $N_2O$  relative to  $N_{IN}$  and 78 % for 10 % N- $N_2O$  relative to  $N_{IN}$ . The use of eSEA and the redefinition of the traditional EQ to  $\Delta EQ_{new}$  provide the possibility of integrating  $N_2O$  emissions into the overall cleaning performance of a WWTP and therewith balance the effluent quality and the GHG criteria.

## 5.4 Conclusions

In this chapter the advantages of eSEA are used for evaluation of the nitrogen removal performance of WWTPs and the entropy indicator is implemented into the traditional EQ as it is applied in the BSM N°2 software by redefining the traditional EQ to  $\Delta EQ_{new}$ . The main benefits of eSEA are first that use of weighting factors based on experts' estimation of the harming potential of the different nitrogen compounds can be avoided because the several nitrogen compounds in eSEA are distinguished based on their naturally occurring background concentrations in the unstressed hydrosphere and atmosphere. Second, in eSEA, nitrogen compounds such as  $NH_4^+$ , SBN, and PBN can be differentiated. Nitrite,  $NO_2^-$ , a byproduct of the nitrification process could principally also be included and emissions of  $N_2O$  can be considered for a more comprehensive assessment of the nitrogen removal performance. Thus, the effluent quality is balanced with the GHG  $N_2O$  in the context of the overall cleaning performance. The newly defined parameter,  $\Delta EQ_{new}$ , thus allows a more comprehensive and therefore, a more precise evaluation of the WWT performance by considering the characteristics of the wastewater and the distribution of all nitrogen compounds in the effluent, the off-gas, and the sludge. The calculation of eSEA can easily be modeled within the BSM N°2. That way, the cleaning performance expressed by  $\Delta EQ_{new}$  can be provided for every time step and reflect the fluctuations within the evaluation period. This work also demonstrates that realistically expectable  $N_2O$  emissions have only a moderate influence on the overall cleaning performance. However, as already recommended by other researchers (Corominas, et al., 2012), a more detailed model for the estimation of

N<sub>2</sub>O emissions is required to predict the N<sub>2</sub>O production during the entire WWT process more realistically.

## 6 Summary of results and conclusions

This thesis aimed at extending SEA to chemical compounds thus offering the eSEA as a new evaluation tool for the assessment of the concentrating power, respective, the extent of dilution of systems where the chemical specification of the processed substances is of particular importance. Nitrogen is an element, which appears in various chemical forms that differ considerably in their environmental harming potential. Although we are far from nitrogen scarcity we should still strive for an efficient nitrogen management for three main reasons. Many nitrogen losses to the hydrosphere, the atmosphere and to the soil can cause severe harm to the environment. From the perspective of a sustainable resource management, reducing losses of substances to the environment should be aspired wherever possible thus increasing the availability of the substance for further use. The availability of nitrogen and therefore, the possibility of nitrogen recycling can finally be more cost-effective than purchasing new nitrogen sources such as fertilizer. Nitrogen budgets were therefore used in this work to test the potential of eSEA for evaluation of farming regions and WWTPs, two systems that are highly relevant to water resources.

Chapter 2 presents the extension of SEA to chemical compounds based on application of eSEA to a hypothetical system consisting of a crop farming region. The results show that the optimal utilization of nitrogen (maximum yield) occurs with low entropy production and that significant losses of nitrogen to the environment produce entropy. The emission of a quantity of, for example,  $\text{N}_2\text{O}$  generates more entropy than the emission of the same quantity of  $\text{NH}_3$  due to the significantly lower natural background concentration of  $\text{N}_2\text{O}$  in the unstressed atmosphere. For the same reason, more entropy is produced after the discharge of  $\text{N}_{\text{org}}$  to surface water and groundwater than it is after the release of  $\text{NO}_3^-$ . The main advantage of eSEA is the consideration of all sorts of nitrogen compounds that occur during the processes of such a farming region thus providing a comprehensive assessment of the nitrogen performance. The findings indicate that statistical entropy may have the potential to become a meaningful indicator for the quality of regional substance management.

In Chapter 3, eSEA is used to assess the nitrogen performance of two different Austrian catchments, the Wulka and the Ybbs, and of entire Austria. Current evaluation procedure for nutrient budgets is based on the quantification of the efficiency of the particular nutrient with respect to its conversion into the food products, like shown using

the example of the nitrogen use-efficiency (NUE). The NUE, in fact, indirectly indicates the losses to the environment because apparently, the nitrogen that is not converted into the food products will be lost to the surroundings. This is demonstrated based on the nitrogen management of the Wulka and the Ybbs catchment. The NUE of the regions clearly shows that the nitrogen conversion into the food products of the Wulka catchment is significantly more efficient than that of the Ybbs catchment. The eSEA results also reveal that the nitrogen management of the Wulka catchment is more favorable compared to the Ybbs catchment primarily as a result of the lower level of nitrogen emissions to the atmosphere and to groundwater. However, the NUE is limited for a comprehensive assessment of the nitrogen performance of a particular region because it only considers the total nitrogen neglecting the different nitrogen compounds and their transfer to the several environmental compartments. This limitation becomes obvious when comparing the nitrogen performance of Austria state-of-the-art nutrition and Austria optimized nutrition based on the recommendation by the German Nutrition Society. Different research groups have proven the multiple benefits of such an improved diet. The NUE however improves only marginally if the nitrogen budget is adapted to the new diet. This difference even becomes insignificant if the uncertainty of the input data is taken into account. The eSEA, in turn, proves that such a healthy, balanced diet leads to a more favorable nitrogen management due to fewer losses of nitrogen compounds to the environment. Thus, statistical entropy is a more comprehensive and reliable indicator for assessing nitrogen budgets than the NUE. A general challenge in the evaluation of agricultural nutrient budgets is missing or poor information about the data quality. Uncertainties can be very high thus affecting the conclusions of an assessment procedure.

In Chapter 4 eSEA is used for the assessment of the nitrogen removal performance of 56 Austrian WWTPs. Current evaluation procedure for WWTPs is based on the estimation of concentrations of water quality relevant substances in the effluent. Additionally, removal rates are reported, such as the nitrogen removal rate. The nitrogen removal rate is useful for a fast assessment of the nitrogen removal performance of a particular WWTP and in many cases a high nitrogen removal rate will coincide with a high reduction in statistical entropy,  $\Delta H$ . However, as shown in this thesis, sometimes the nitrogen removal rate can be misleading because it only considers the total nitrogen in both the wastewater and the effluent. The eSEA offers a more comprehensive assessment of the nitrogen removal performance than the nitrogen removal rate because it considers the different nitrogen compounds including

gaseous emissions, the distribution of nitrogen in the wastewater, effluent, off-gas, and sludge, and the dilution of these emissions in the environment. Application of eSEA rewards WWTPs that transform nitrogen compounds from the wastewater into harmless (or less harmful) species, such as  $N_2$  or  $NO_3^-$ , for instance. Furthermore, the eSEA results are set in relation to the energy consumption and the costs responsible for the nitrogen treatment. Comparison of the energy-efficiencies and the cost-effectiveness of small WWTPs responsible for pollution loads less than 50,000 PE and large WWTPs that treat wastewaters with pollution loads higher than 50,000 PE reveals that energy-efficiency does not necessarily imply cost-effectiveness and that small WWTPs can operate as energy-efficient as large plants and in some cases likewise cost-effective. These findings can have important implications for the planning and design of WWT facilities.

In Chapter 5, eSEA is implemented into the effluent quality index, EQ, of the WWT simulation software, the Benchmarking Simulation Model, BSM N°2. Therefore, the traditional EQ is restructured to  $\Delta EQ_{new}$ . The limitations of the EQ are that it does not differentiate  $NO_3^-$  from  $NO_2^-$ ,  $NH_4^+$  from  $N_{org}$ , and it does not include emissions of  $N_2O$ . Due to implementation of eSEA for the assessment of the nitrogen removal performance the newly defined parameter,  $\Delta EQ_{new}$ , allows a more comprehensive and therefore, more precise evaluation of the WWT performance by considering the cleaning performance of the WWT including the emission of  $N_2O$ . It is found that the denitrification process generates  $N_2O$  emissions in the range of 0.34% to 0.44% relative to the total nitrogen in the wastewater. These  $N_2O$  emissions have only a minor impact on the eSEA results, and hence, also on  $\Delta EQ_{new}$ .

In eSEA, one determining factor for the quantification of the dilution of nitrogen compounds in the hydrosphere is the calculation of theoretical diluting masses. However, the water masses that are actually available for dilution are not taken into account. From an ecotoxicological point of view emission of  $NH_4^+$ ,  $NO_3^-$ , and  $NO_2^-$  will less affect a big river because it contains enough water to dilute these emissions up to their corresponding background concentrations. A small river, in turn, may not yield enough water for dilution thus leading to eutrophication and/or lethal effects to water organisms. Similarly, pollution of a groundwater with a high renewal rate will be less critical than that of a groundwater with a small renewal rate. In addition to dilution, running waters show self-cleaning capacities in form of biological decomposition, oxidation and reduction processes that depend on parameters such as the flow



velocity, the characteristics of the river channel, temperature, pH, water depth, and solar radiation. For eSEA, such self-cleaning capacities do not play any role, either.

The findings of this doctoral thesis further reveal that emission of  $\text{N}_2\text{O}$  has only a small impact on the overall nitrogen removal performance of WWT facilities. In fact,  $\text{N}_2\text{O}$  in the atmosphere has hardly any toxicological significance for humans. Yet, it has great importance as GHG and for the  $\text{O}_3$  depletion. Due to  $\text{O}_3$  depletion high energy UV radiation can get through causing damaging long-term consequences for life on earth. In eSEA the significance of  $\text{N}_2\text{O}$  emissions might therefore not be adequately represented. As a consequence of the little impact of  $\text{N}_2\text{O}$  emissions on the cleaning performance WWTP operators might not be motivated to apply measurements to reduce  $\text{N}_2\text{O}$  emissions. At the same time, the impact of  $\text{N}_2\text{O}$  emissions should not be overestimated. In the beginning of WWT neither nitrification nor denitrification were applied. As a consequence, no  $\text{N}_2\text{O}$  was generated but on the other hand high concentrations of  $\text{NH}_4^+$  were discharged into the rivers. If the denitrification process was omitted less  $\text{N}_2\text{O}$  would be generated but relatively high concentrations of  $\text{NO}_3^-$  would then reach the rivers. Any assessment of the nitrogen removal performance should therefore secure that state-of-the-art WWT applying both nitrification and denitrification results more favorable than WWT without nitrification, denitrification or both.

Nitrogen is only one relevant nutrient regarding both farming regions and WWTPs. For a comprehensive evaluation of nutrient budgets in farming regions it would be necessary to include the phosphorus performance, for instance. For WWTPs, parameters such as phosphorus, COD, BOD, SS, heavy metals, and eventually pharmaceutical compounds should also be considered. Thus, the extension of SEA to multiple elements and, in consequence, the extension of eSEA to multiple chemical compounds is recommended for future research.

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## List of all indices and parameters

$H$	Statistical entropy according to Shannon's definition
$\Delta H$	Change in statistical entropy representing the concentrating power ( $\Delta H < 0$ ) or the diluting extent ( $\Delta H > 0$ ) for nitrogen
$H_{\max}$	Maximum occurring statistical entropy
$H_{\text{IN}}$	Statistical entropy for all incoming nitrogen compounds in the region
$H_{\text{IN,rel}}$	Relative value of statistical entropy ( $H_{\text{IN}} / H_{\max}$ ) for all incoming nitrogen compounds in the region
$H_{\text{OUT}}$	Statistical entropy for all nitrogen compounds that leave the region
$H_{\text{OUT,rel}}$	Relative value for statistical entropy ( $H_{\text{OUT}} / H_{\max}$ ) for all nitrogen compounds that leave the region
$H_{\text{noWT}}$	Statistical entropy for all nitrogen compounds in case wastewater is directly discharged into the receiving waters
$H_{\text{afterWWT}}$	Statistical entropy for nitrogen after wastewater treatment
$P_i$	Probability of an event $i$
$\dot{M}_i$	Mass flow, e.g., rainwater in kg/ha/a
$i$	Index for mass flows, e.g., rainwater
$k$	Number of all input mass flows $i$
$c_i$	Concentration of a substance $i$ , e.g. kg cadmium per kg mass-flow
$c_{im}$	Nitrogen concentration of nitrogen compound $m$ in mass flow $i$ , e.g., kg N-NH <sub>4</sub> <sup>+</sup> per kg groundwater
$m$	Index for nitrogen compounds, e.g., NO <sub>3</sub> <sup>-</sup> , NH <sub>4</sub> <sup>+</sup> , N <sub>2</sub>
$r$	Number of different nitrogen compounds $m$ in the input
$\dot{X}_{im}$	Nitrogen load for nitrogen compound $m$ in material flow $i$ , e.g., kg N-NH <sub>4</sub> <sup>+</sup> in kg groundwater per hectare per year

$m_i$	Specific mass for material flow $i$ , e.g., kg groundwater per kg total nitrogen throughput of the process
$X_{im}$	Specific nitrogen load, e.g., kg N-NH <sub>4</sub> <sup>+</sup> per kg total nitrogen of the output
$s$	Number of different nitrogen compounds $m$ in the output
$l$	Number of all outgoing mass flows
$m'_{im}$	Diluting mass from mass flow $i$ for nitrogen compound $m$
$c'_{im}$	Corresponding concentration term for nitrogen compound $m$ in mass flow $i$ to diluting mass $m'_{im}$
$c_{im,geog}$	Background concentration corresponding to nitrogen compound $m$ in environmental compartment $i$ , e.g., kg N-NH <sub>4</sub> <sup>+</sup> per kg groundwater
$\min(c_{j,geog})$	Smallest occurring corresponding background concentration, e.g., N-N <sub>org</sub> concentration in groundwater