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Life-Cycle Assessment of Neonicotinoid Pesticides

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Abstract

Neonicotinoid pesticides have been an increasing focus of the environmental community, due to their potential impacts on bee populations and other important insects. The goal of this study was to develop a life-cycle assessment (LCA) approach that could be used to quantify the environmental impacts of two common neonicotinoid pesticides, Imidacloprid and Thiamethoxam. In order to develop the LCA study, an equivalent scenario was created for each pesticide that incorporated data on the production of each pesticide, followed by transportation to a model farm site in Brazil and application with an in-furrow pesticide application system. Data sources for the materials and energy used, combined with resulting emissions to air, water, and soil, were gathered from peer-reviewed literature, government reports, life-cycle inventory databases, and other sources. The SimaPro LCA modeling platform was used to assess the impacts of each life cycle on Human Health and Ecosystem Quality, according to the Impact 2002+ method. Results indicate that important differences exist between the pesticide life cycles, with Thiamethoxam resulting in lower LCA impacts in both impact areas and most mid-point categories under study. Pesticide production impacts varied by over an order of magnitude between the Imidacloprid and Thiamethoxam, while pesticide transport was determined to be a negligible source of environmental impact in both systems. Pesticide application activity using tractors was a larger contributor to Human Health and Ecosystem Quality impacts than the ultimate effect of the pesticide emission to the environment, which should be an area of further study to confirm this finding with the pesticides in question and also to focus impact on the application systems as a potential method of reducing environmental impact, in addition to pesticide toxicity.

Keywords: Neonicotinoid; Pesticide; Imidacloprid; Thiamethoxam

Introduction

Insecticides are a class of pesticides used to kill, harm, or repel different species of insects. They act in different ways in organisms based on their active ingredients. For instance, corn plantations commonly use insecticides that have organophosphates and carbamate as the active ingredient, which acts on the enzyme acetylcholinesterase within an insect nervous system. In many cases, these standard insecticide products are being phased out for a new class of insecticide known as neonicotinoids, which use nicotine as the active ingredient. Neonicotinoid compounds interact with nicotinic acetylcholine receptors (nAChR) of the central nervous systems of insects [1]. Nicotine acts in an insect's system in the same way that it acts in the human body. However, neonicotinoids are more toxic for invertebrates than they are to mammals, birds and other higher organisms. Neonicotinoids became popular because of their high water solubility, which makes their soil application travel through the entire plant. Nowadays, neonicotinoids are one of the most widely used class of insecticides for controlling sucking insects and soil insects. In 2004, the worldwide annual usage of neonicotinoids was approximately 11-15% of the total insecticides in the market [2]. Different generations of neonicotinoids have been created over time. They have the same principle of action in the nervous system; however, the specific active ingredients are different. The first generation of this pesticide class used was 1-(6-chloro-1,3-thiazol-5-ylmethyl)-1,3,5-oxadiazinan-4-ylidenene(nitro)amine, known as Imidacloprid. It was first registered for use in the United States by the United States Environmental Protection Agency in 1994. It is the most widely used generation of neonicotinoids, and there are several hundred Imidacloprid-based products for sale in U.S. In 2006, the worldwide sales of those products were near $1.6 billion [3]. In 2009, Imidacloprid was applied to hundreds of thousands of acres in California, one of the most used pesticides that time [4]. Some commercial examples of this class of insecticide are Gaucho® (seed treatment), Admire® (soil application), Provado® (foliar application), Merit® (turf and ornamental use) and Premise® (termite control). Most are produced by Bayer Company [5]. The second generation of neonicotinoids is known as Thiamethoxam. The most active ingredient is 1-(6-chloro-1,3-thiazol-5-ylmethyl)-1,3,5-oxadiazinan-4-ylidenene(nitro)amine. It was first approved in 1999 for use as an antimicrobial wood preservative and as a pesticide. The main products of this generation are produced by Syngenta Company, including Platinum®, Actara®, Centric®, Cruiser®. Flagship® and Helix® among others [6]. Those products were introduced in the US market in 2001 [5]. Even though neonicotinoids have different effects in mammals and insects, they are a source of large concerns in the world. Many countries in the EU and around the world have banned the use of these chemicals. This is primarily because some classes of neonicotinoids have been demonstrated to be quite toxic for bees and other beneficial insects. Many studies show that bee disorders are being caused by the contamination of this type of insecticide in plant nectars that feed bees [7]. These beneficial insects are responsible for more than $15 billion in crop production in United States annually [8]. Many studies are being developed to analyze the actual risk of neonicotinoids in those insects. Also, neonicotinoids can persist in the soil for years, so it may contaminate other plants and non-target species over time. Pesticides may contaminate water, soil, fish, and other living

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species [9,10]. One important study method used to assess the potential environmental impacts of products and systems is Life Cycle Assessment (LCA). This technique has been applied to many different products throughout many different industries, but the generally accepted best practices for LCA consist of (1) rigorously defining the goal, scope, and system boundary of the study, (2) compiling an inventory of the important flows of materials and energy throughout the product life cycle system boundary, (3) assessing the environmental impacts of this inventory data with a transparent and replicable impact assessment method, and (4) interpreting data to define new study conditions or suggest improvements to the product life cycle [11]. Ideally, an LCA study should be cradle-to-grave, examining environmental impacts throughout the product life cycle, from extraction of raw materials, to product assembly, use, and finally to disposal of wastes. In this article, a life cycle assessment method is used to quantify the environmental impacts of production, transport, and usage of the active ingredients in two common neonicotinoids, Imidacloprid and Thiamethoxam. SimaPro 8.0 LCA software was used in conjunction with the Ecoinvent life cycle inventory database [12] to construct product life cycles for both pesticide active ingredients and assess the impacts, in terms of regards of human health and ecosystem quality. Additional discussions regarding the toxicity and persistence in the environmental after their application, and how this would impact the environmental impacts of these products, are also offered based on a literature review of their use in typical cultivation systems.

Study Methods

Goal and scope

The goal of this study is to determine the environmental impacts of two different generations of neonicotinoids, Imidacloprid and Thiamethoxam, resulting from their production, transport, and ultimate application in the environment. The environmental impacts being assessed are terrestrial ecotoxicity, aquatic ecotoxicity, and human health impacts. The functional unit used in this experiment is 1 kg of insecticide applied to land. The system boundary includes production and transport of materials and energy used in the production, transport, and application stages of each pesticides life cycle. Figure 1 displays the system boundary along with key inputs that are described in more detail below. In each scenario for the two different pesticides, the application stage is assumed to take place on a farm in the State of Ceará, Brazil, as a common point of reference.

Life cycle inventory

To accomplish this life cycle assessment study, information on the inputs of materials and energy related to the full product life cycles was collected from a variety of peer-reviewed publications, government reports, and other sources. The following sections summarize the key inputs of materials and energy that have been considered in each stage of the insecticide life cycle, along with key assumptions relating to the development of this input data.

Production stage: Imidacloprid production was summarized in a 2006 article originating from the Institut fur Lebensmittelchemie in Germany [13], and this information is utilized in this study to model the production of this pesticide. There are alternate routes to production [14], but few studies include as much detail on the synthesis as the Schippers and Schwack work [13]. The synthesis is divided in five steps with an overall yield of 10%. In the beginning, ammonia is used to react with coumalic acid methyl ester to form the hydroxyl nicotinic acid. This is the cheapest way to start the production of the insecticide. All products and their amounts are specified in Table 1, with an estimated production of 1.01 grams of Imidacloprid. These amounts were scaled up proportionally to the reported yield in order to model a production of 1 kg in the life cycle model. In the synthesis procedure, some reactions need heating and cooling as part of the process. In order to estimate the energy usage required for these steps in a commercial application, an assumption was made that heat can be provided or removed from the system via a heat exchange system with an efficiency of 80%, using water as the exchange fluid. Some reagents utilized in this synthesis method were not available in the Ecoinvent database, and in these cases similar products were used or the creation of the required reagents was modeled using required inputs when present within the Ecoinvent database. These assumptions have been noted in Table 1. Reagents used just to wash or extract a chemical were assumed to require 50 mL per washing step in this production process, unless otherwise indicated in Table 1. Thiamethoxam synthesis was modeled according to the route described in a paper from Syngenta Crop Protection researchers [15]. The materials and energy requirements for synthesis of 220 g of Thiamethoxam at 98% purity are presented in Table 2, and are scaled up to a production of 1 kg with our LCA model to be consistent with the functional unit of this study. Similar assumptions are used in this production unit operation as were used for Imidacloprid, namely that heat exchangers can or remove heat from the system while operating at an efficiency of 80%, and the specific heat of water is used to represent the solution heat capacity and working heat exchange fluid. The main compound used in this production system is dimethyl carbonate. It is used in the production in different steps, however in Table 2 it is shown in a single amount.

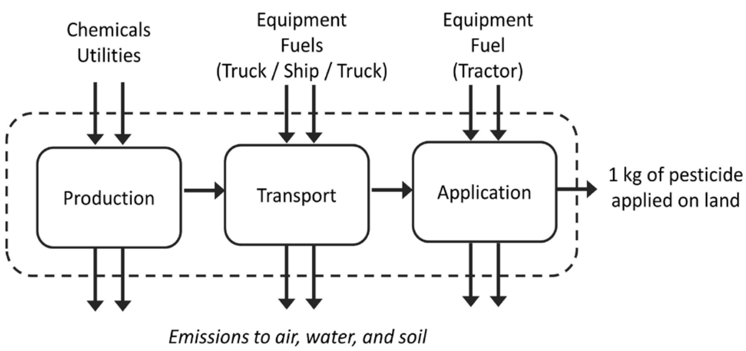

Figure 1: General description of LCA system boundary for both pesticide scenarios under study. Inputs at each stage are normalized to ultimate application of 1 kg of the pesticide to agricultural land. Emissions to air, water, and soil are used to calculate environmental impact according to common LCA methods.

Item	Amount	Comments
Chemicals		
Coumalic Acid methyl ester	4 g	Coumalic acid methyl ester is synthesized from malic acid, using fuming H_2SO_4 and absolute methanol. This compound was created in Ecoinvent database according to Smith and Wiley [16].
Ammonia	10 g	
Sodium hydroxide (21%)	14.7 g	Density=1.222 g/mL
Hydrochloric acid	12.2 g	Required amount necessary until pH of 4.5. Assumed equivalent volume to NaOH. Density=1.017 g/mL
Phosphorus pentachloride	3.56 g	
Phosphorus oxychloride	2.80 g	Utilized Phosphoryl chloride in Ecoinvent database. Density=1.645 g/mL
Sodium borohydride	700 mg	Utilized sodium tetrahydridoborate in Ecoinvent database.
Ethanol	150 mL	Density=0.789 g/mL, mass=118.35 g.
Sodium hydroxide (0.01N)	1.5 mL	Density=1.011 g/mL, mass=1.52 g.
Sodium chloride	50 mL	Assumed amount to treat the residue.
Diethyl ether	50 mL	Assumed amount to extract the organic phase.
Anhydrous sodium sulfate	0.94 g	Assumption: used for drying and can contain $7H_2O$ when fully hydrated, 1 mol of sodium sulfate is needed to remove 10 mols of water in each mol of product
Thionyl chloride	0.79 g	Assumption: In chloroform, and 1 mol of thionyl chloride (118.97 g/mol) is necessary to react with 1 mol of N-(6-chloropyridin-3-yl)methanol (143.57 g/mol) that has 0.95g grams.
Potassium carbonate	3.9 g	
Acetone	100 mL	
Ethylenediamine	0.462 g	Synthesis was created in SimaPro. 60.10 g/mol. 1 mol necessary to produce 1 mol of 2-nitroiminoimidazoline.
$(NH_2)_2CNNO_2$	0.799 g	Used in the production of 1 gram of 2-nitroiminoimidazoline (130.11 g/mol). Ecoinvent reference: nitro compound.
Ethyl acetate	100 mL	Assumption of the amount to extract the solution (3 times).
Energy[a]		
Heat to 48°C	1.69 kJ	Used the total mass (14 g), starting at room temperature
Heat to 100°C	7.81 kJ	Assumptions: Heated from 48°C. The total mass is the sum of all compounds in the solution at the moment.
Heat to 75°C	2.28 kJ	Assumptions: The mass of the previous product (2.33 g), and the both phosphorous compounds are used as the total mass. Starting at room temperature.
Heat to 120°C	2.05 kJ	Assumptions: The same total mass was used as previous. Heated from 75°C.
Cooling to 4°C	14.22 kJ	Assumptions: The total mass is the previous product+all compounds added. Initial temperature=room temperature.

a: In all calculations of required energy at each heating/cooling phase, the specific heat of water was assumed, along with a heat exchanger efficiency of 80%.

Table 1: Material and Energy Requirements for 1.01 g of Imidacloprid Production.

Item	Amount	Comments
Chemicals		
Dimethyl carbonate (DMC)	1050 g	Assumption: Created in SimaPro using Ecoinvent data for reagents of carbon monoxide, oxygen, and methanol according to Tundo and Selva [17]. This amount of DMC is used in different parts of the procedure.
3-methyl-4-nitroimino-perhydro-1,3,5-oxadiazine	184 g	Assumption: Used generic Diazine Compound present within Ecoinvent database as substitute.
2-chloro-5-chloromethylthiazole	168 g	Assumption: Created in Ecoinvent database using information present in Decker [18]
Tetramethylammonium hydroxide pentahydrate	4 g	Assumption: Created in Ecoinvent database using information present in Walker [19]
Potassium carbonate	242 g	
Water	900 g	Deionized water
Hydrochloric acid	260 g	
Energy[a]		
Heat to 65°C	157.54 kJ	Assumptions: Mass: sum of all compounds for the first mixture. Initially at room temperature.
Heat at 62°C to 68°C	18.73 kJ	Assumptions: The sum of all compounds mass in the mixture are used in the calculation. Initial temperature=62°C.
Cool to 47°C	65.55 kJ	Assumptions: When 99% of product is formed, the mixture is cooled. Total mass of reagents used as mass.
Heat to 65°C	111.04 kJ	Assumptions: The mass used was the sum of a possible product of 200 g+the water and hydrochloric acid. Initial temperature is 45°C.
Heat to 65°C	125.7 kJ	Assumptions: The mass used was the final mass after the heating. The initial temperature was room temperature after waiting for phase separation.
Cool at 65°C to 5°C	188.55 kJ	Assumptions: The mass used was the final mass after the heating.
Cool at 5°C	1 kWh	Electricity used to keep the mixture temperature at 5°C for 1 hour, 1 kW power requirement
Vacuum at 70°C	176.77 kJ	Assumptions: the mass used was the sum of a possible product of 200 g+the water and 300 g of DMC. Initial temperature is room temp.

a: In all calculations of required energy at each heating/cooling phase, the specific heat of water was assumed, along with a heat exchanger efficiency of 80%.

Table 2: Material and Energy Requirements for 220 g of Thiamethoxam Production.

	Imidacloprid	Thiamethoxam	Comments
Production Facility	Grundhof, Schleswig-Holstein State, Germany	Corlim, Goa State, India	Thiamethoxam produced at Syngenta Agro Chemicals facility [20] Imidacloprid is primarily produced in Germany, with minor amounts produced at other locations [21,22]
Distance to Port Facility	17 km Flensburg	32 km Mormugao	Truck transport assumed in Ecoinvent (16-32 t lorry)
Ocean Shipping Distance	6043 nm	9481 nm	Distance between ports determined via http://ports.com, long-distance transoceanic ship transport assumed in Ecoinvent (Distances presented in nautical miles)
Distance to Agricultural Site	150 km	150 km	Truck transport assumed in Ecoinvent (16-32 t lorry)

Table 3: Key inputs and assumptions for Transportation stage of pesticide life cycles.

Transportation stage: Inputs and assumptions for the transportation stage can be seen in Table 3, where 1 kg of the pesticide was moved according to the following multi-modal transportation scheme. Each of the neonicotinoid pesticides are produced in commercial quantities at locations far away from the farm field in Ceará where the pesticides are used in this scenario, which reflects the global supply chains that many chemicals currently have. For each pesticide, the predominant production facility was assumed according to available public information. Transportation from the production facilities in India (Imidacloprid) and Germany (Thiamethoxam) to the nearest local commercial scale port facility was accomplished with truck transportation profiles available in the Ecoinvent database, followed by shipping from the ports in the respective countries to the city of Fortaleza. Final truck transportation to a farm field in central Ceará was assumed to be equivalent in each scenario.

Application stage: In the application stage, this LCA study attempts to quantify the impacts associated with the actual application activity required to spread the pesticides on a farm field, along with the resultant impacts of that soil application. The use of machinery to apply insecticides to the field is included in the study. The most common way to apply neonicotinoids in the environment is using the in-furrow method with tractors, which is faster and safer for workers. This is possible because both pesticides area able to translocate throughout the plants from the roots. AmTide Imidacloprid 2F, a commercial product of Imidacloprid, is applied in a maximum rate in of 0.35 kg / ha in potatoes and other tuber-based agricultural cultivation systems [23]. Thiamethoxam needs to be applied in a rate of 0.14 kg/ha of soil [24] in for cultivation of potatoes and other tubers. Using a consistent tractor fuel usage rate of 2.6 L diesel/ha of soil [25], it is possible to calculate the tractor fuel requirements for spreading 1 kg of each pesticide. To account for the other inputs of materials and energy (tractor production, equipment use) and other engine emissions, a pesticide application process profile in Ecoinvent was modified to include the appropriate level of fuel consumption and fuel combustion per hectare as indicated in Ref. [25], and used to model the overall application process. After being applied in the environment, pesticides generally move into soil and water at variable rates, where they may interact with several different non-target species, and this is a subject of much recent research interest. The half-life of Imidacloprid in soil has been reported in different conditions. On average, it is 130 days, but it can increase with the pH or absence of light [26]. For Thiamethoxam, the half-life is 47-54 days in presence of light [27]. It means that both pesticides persist in the soil for a long time so it can interact with other plants or living species in the soil. The study of hydrolysis of those insecticides is a useful method to analyze their persistence and potential contamination of water bodies. After application, neonicotinoids can reach either lakes or groundwater. Sunlight makes the hydrolysis faster, however Imidacloprid can persist in the water for more than 30 days in pH 7 [26] and Thiamethoxam can be stable at pH 5 and persist for 580 days in pH 7 [27]. As insecticides are persistent in the soil and water, they can interact with different living species. Neonicotinoids act in different ways in mammals and insects, but they can be toxic to humans and mammals in general. Many studies show the lethal dose in rats or rabbits as model species. Once in the environment, Imidacloprid and Thiamethoxam can get in human bodies from different routes, such as oral, dermal, and inhalation, with potentially different toxic effects from different routes of exposure. Using rats as an example, the lethal dose for 50% of exposed animals (LD_{50}, a common toxicity metric) via oral exposure is 450 mg/kg for Imidacloprid [28]. For Thiamethoxam, the LD_{50} is 100 mg/kg [29]. They are classified as moderately toxic. Some signs of toxicity with Imidacloprid in humans are drowsiness, dizziness, vomiting, disorientation, increased heart and respiratory rates, and fever. However, when neonicotinoids contaminate foods, they generally do not represent a risk for human health due to the low dosage and relatively rapid excretion. In regards to carcinogenicity, Imidacloprid has been classified into Group E, meaning there is no evidence of carcinogenicity in studies with rats [30]. However, a study of human lymphocytes exposed to greater than 5200 μg/ml of Imidacloprid demonstrated a slight increase in chromosome abnormalities *in vitro* [31]. Studies for Thiamethoxam show that it does not have a carcinogen risk for humans and rats too [32]. In bees or other insects, the impacts can be more serious. Since bees are more similar to the target insects of neonicotinoids, the lethal dose for them is smaller. Because of it, many disorders are being caused in different cultivations around the world. Pesticides can affect bees though direct contact or though ingestion of pollen or nectar. The lethal dose needed to kill 50% of bees is 0.0037 μg/bee of Imidacloprid via oral and 0.0179 μg/bee via contact [33]. For Thiamethoxam, the LD_{50} for honey bees is 0.005 μg/bee via oral and 0.024 μg/bee via contact [34]. Thus, both classes of insecticides are classified as highly toxic to honey bees. Since Imidacloprid and Thiamethoxam are not present within the set of pesticides available within the current Ecoinvent database or the environmental impact assessment methods available to quantify the ecosystem or human health impacts, a similar insecticide available within the LCA modeling platform was used as a proxy. Relative toxicity values between the three pesticides were then used to simulate the appropriate exposure impact in land, water, and air. Fenvalerate is a pyrethrin insecticide, and is considered moderately toxic to mammals and highly toxic to insects, including bees. The LD_{50} for Fenvalerate in rats is 451 mg/kg, which is very similar to Imidacloprid and 4.5-fold higher than Thiamethoxam. The assumption used for this study followed the guidance of available rat exposure data, that 1 kg of Imidacloprid emission to the environment could be reasonably represented by 1 kg of Fenvalerate emissions, while 4.5 kg of Fenvalerate emissions would have to be used to represent 1 kg of Thiamethoxam emissions to the environment. Fenvalerate is classified as highly toxic to bees with a reported LD_{50} of 0.017 μg / bee, similar to the neonicotinoid pesticides [35].

Impact assessment

To analyze different environmental impacts, the SimaPro LCA tool includes several established impact assessment methods that characterize different aspects of environmental impact. The method used in this experiment is Impact 2002+. This methodology proposes a feasible implementation a combined midpoint/damage approach, linking all types of life cycle inventory results via 14 midpoint categories to 4 damage categories [36], which is explained in greater detail in other resources. For this study, the two endpoint damage categories being assessed are ecosystem quality and human health impacts. Ecosystem quality is quantified by combining multiple midpoint indicators and is expressed in terms of Potentially Disappeared Fraction (PDF) of species over a certain area per year, in this case PDF/m^2/yr. Human Health impacts are also quantified by combining several midpoint indicators, and are cumulatively expressed in terms of Disability-adjusted Life Years (DALY), accounting for human health in terms of changing mortality and morbidity related to environmental impacts.

Results and Discussion

A summary of endpoint results for the life cycle Human Health and Ecosystem Quality impacts of each pesticide can be seen in Table 4. Results are separated into each stage of the life cycle, and several of the most impactful items in each stage are shown as well. Figures 2 and 3 display the results of the midpoint indicators that contribute to the ultimate quantification of the two endpoint categories. Because each of the midpoint categories are assessed using different units, a normalization procedure was performed in order to display them on the same Figures with each other. Life cycle results for Imidacloprid in each of the midpoint categories were normalized to a value of 1.0, to remove the influence of different units. Life cycle results for Thiamethoxam were also normalized on the same basis, in order to facilitate comparison between the two pesticides across a range of midpoint categories.

Imidacloprid life cycle

The production stage of the imidacloprid life cycle is a significant source of environmental impacts, especially concerning Human Health, where roughly 90% of the life cycle impacts occur (7.11×10^{-4}

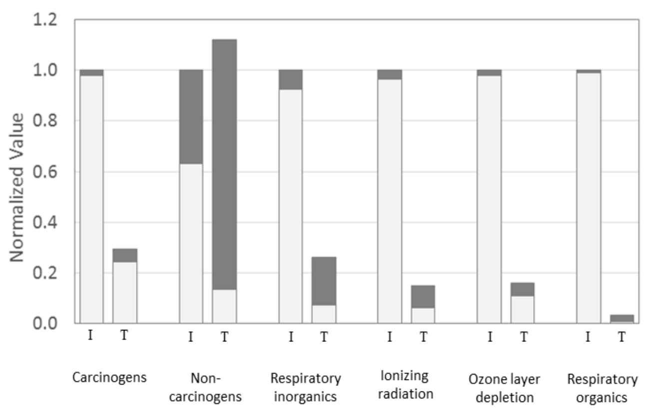

Figure 2: Midpoint indicator results for categories that contribute to Human Health endpoint impact metric, using a functional unit of 1 kg pesticide. Data for different midpoint indicators are measured according to different units, but here they have been normalized by normalized the life cycle impact value of Imidacloprid ("I" columns) to a value of 1.0. Thiamethoxam ("T" columns) values for each midpoint category were normalized according to the Imidacloprid scale, to illustrate the comparison between the two pesticides. In all columns, light colored bars represent impacts for the Production stage and dark colored bars represent impacts from the Application stage. The Transportation stage is too small to be observable in all categories.

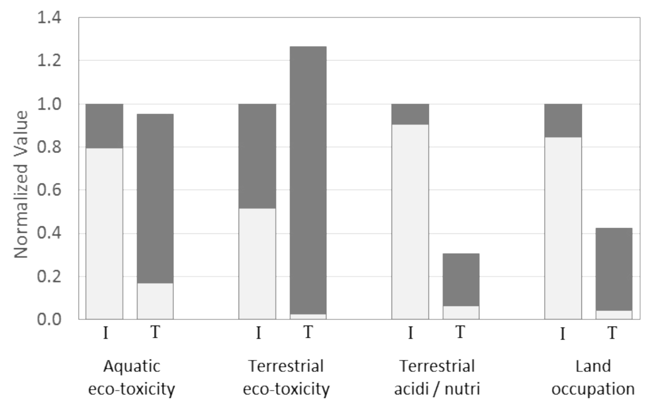

Figure 3: Midpoint indicator results for categories that contribute to Ecosystem Quality endpoint impact metric, using a functional unit of 1 kg pesticide. Data for different midpoint indicators are measured according to different units, but here they have been normalized by normalized the life cycle impact value of Imidacloprid ("I" columns) to a value of 1.0. Thiamethoxam ("T" columns) values for each midpoint category were normalized according to the Imidacloprid scale, to illustrate the comparison between the two pesticides. In all columns, light colored bars represent impacts for the Production stage and dark colored bars represent impacts from the Application stage. The Transportation stage is too small to be observable in all categories.

	Imidacloprid		Thiamethoxam	
Stage	Human Health (DALY)	Ecosystem Quality (PDF / m^2 / yr)	Human Health (DALY)	Ecosystem Quality (PDF / m^2 / yr)
Production	**7.11×10^{-4}**	**98.21**	**7.80×10^{-5}**	**5.70**
	ethyl acetate 2.03×10^{-4}	*ethyl acetate 34.0*	*coumlic acid 4.35×10^{-5}*	*diazine 2.08*
	diethyl ether 1.78×10^{-4}	*diethyl ether 25.7*	*diazine 1.55×10^{-5}*	*coumalic acid 2.04*
	acetone 1.01×10^{-4}	*NaCl 12.2*	*dimethyl carbonate 7.95×10^{-6}*	*dimethyl carbonate 0.71*
Transport	**1.72×10^{-7}**	**0.02**	**2.59×10^{-7}**	**0.03**
Application	**6.37×10^{-5}**	**72.0**	**1.61×10^{-4}**	**184.0**
	tractor use 6.23×10^{-5}	*tractor use 69.5*	*tractor use 1.55×10^{-4}*	*tractor use 173*
	pesticide emission 0.14×10^{-5}	*pesticide emission 2.5*	*pesticide emission 0.06×10^{-4}*	*pesticide emission 9.0*
Total	**7.75×10^{-4}**	**170.24**	**2.40×10^{-4}**	**189.73**

Table 4: Life cycle endpoint results for Human Health and Ecosystem quality impacts (1 kg basis).

DALY). These large impacts at the production stage stem from the reliance of pesticide production on organic chemicals such as ethyl acetate or acetone to serve as solvents or washing agents for various parts of the production process. In addition to these organic agents, the NaCl used in the production stage also contributes strongly to the overall Ecosystem Quality damage of the life cycle. The small amounts of heating and cooling required for the various steps of the production stage did not contribute a significant fraction of the overall impact in either endpoint category, less than 1% of the total environmental impact in each category. Transportation of Imidacloprid from its production location in Germany to the farm field in Brazil contributes a negligible amount of impact to both the Human Health and Ecosystem Quality impact metrics. Despite the long voyage, transportation of these products is done on a large scale where 1 kg of pesticide constitutes a trivial portion of the payload in every transport step. Pesticide application is an important part of the life cycle, contributing ~8% of the overall Human Health impact, and 42% of the Ecosystem Quality impact. Interestingly, in both of these impact metrics, the contribution of the tractor use and associated infrastructure for the application of the pesticide was ~30-40X more impactful than the resulting environmental impacts associated with emission of the pesticide into the environment, as modeled by our fenvalerate proxy in the SimaPro modeling tool. Midpoint indicators from the LCA study are presented below in Figures 2 and 3 for indicators contributing to the overall Human Health and Ecosystem Quality results, respectively. In regards to the Human Health impact of Imidacloprid, the production stage was responsible for over 95% of the impacts in 5 of 6 midpoint categories, the only exception being exposure to Non-carcinogenic air pollutants. For the midpoint indicators leading to the Ecosystem Quality result, the impacts were also primarily attributable to the production stage. For Terrestrial ecotoxicity, however, impacts were split roughly evenly between production and application stages, which illustrate the impact on terrestrial organisms from pesticide application to the landscape.

Thiamethoxam life cycle

The LCA results for the Thiamethoxam life cycle (Table 4) illustrate some important differences from Imidacloprid. The production stage of the Thiamethoxam life cycle results in Human Health impacts that are roughly 10X smaller than the Imidacloprid system and Ecosystem Quality impacts that are roughly 20X smaller. The items responsible for the largest impact in the Thiamethoxam life cycle in both impact categories are actual regents or building blocks of reagents in the production system (coumalic acid), as opposed to the organic solvents and washing agents in the Imidacloprid system. Heating and cooling requirements were also shown to contribute less than 1% of the environmental impacts associated with the production stage, similar to the Imidacloprid case. Also similarly, the transportation stage for moving Thiamethoxam from India to Brazil was negligible in the overall product life cycle, compared to impacts associated with production or application. In the application stage, the Thiamethoxam system used more tractor transport and associated materials and energy to spread the pesticide, because the reported dosage per unit land area was lower. Most of the environmental impact at the application stage was again due to the usage of the tractor for pesticide application, as opposed to the impacts associated with Thiamethoxam exposure on the landscape, as modeled by the fenvelarate proxy compound in this study. Overall, the Thiamethoxam life cycle had Human Health impacts that were 70% lower than Imidacloprid (2.40×10^{-4} DALY vs. 7.75×10^{-4} DALY). This general result can be seen in most of the midpoint indicators that contribute to the Human Health impact (Figure 2), where the Thiamethoxam life cycle impacts are generally less than 25% of the comparable midpoint indicator score for Imidacloprid. Non-carcinogenic air pollution is the one midpoint indicator that does not follow this trend, with a higher score for Thiamethoxam that is primarily due to emissions from the production stage, which makes sense due to the higher tractor use assumed for this scenario in our 1 kg functional unit comparison, and engine exhaust is an important source of these air emissions in this life cycle. Total Ecosystem Quality impacts are 11% higher for the Thiamethoxam (189.73 vs. 170.24 PDF / m^2 / yr). In the comparison of midpoint indicators contributing to the Ecosystem Quality impact score (Figure 3), very clear differences are observed between the two pesticides. In the Thiamethoxam life cycle, the production stage is the primary contributor to all Ecosystem-related midpoint indicators, and for Aquatic and Terrestrial Ecotoxicity, the total impacts are equivalent or higher than Imidacloprid.

Alternative functional unit comparison

When conducting an LCA study of a product or process, it is important to keep in mind the function for which that product or system is intended. For a product such as a pesticide, the ultimate service being provided is plant protection from insects. As an alternative to comparing equivalent masses of pesticide over a comparable life cycle, it may also be advisable to make comparisons between pesticides based on an equivalent level of plant protection. To illustrate this alternative comparison, the life cycle scenarios for both pesticides are represented in Table 5 on the basis of 1 ha of field protection, using the same input data and assumptions that have been outlined previously in the article. Because the reported dosage rate for Imidacloprid (the first-generation neonicotinoid pesticide) is 2.48X higher than Thiamethoxam, less Thiamethoxam is needed to provide the same level of plant protection. When the life cycles for each pesticide are normalized to 1 ha of plant protection, the inherent advantage of this lower pesticide requirement is illustrated more clearly. On a 1 ha equivalent basis, the Thiamethoxam life cycle is 87% lower in Human Health impact and 45% lower in Ecosystem Quality, compared to the Imidacloprid life cycle. As opposed to the data presented in Table 4, in this alternative LCA scenario the impacts associated with pesticide application are nearly equivalent, because each case assumes tractor usage for 1 ha of pesticide application, with minor differences due to toxicity impacts of the pesticides after application. Many of the same general points about the two pesticide

	Imidacloprid		Thiamethoxam	
Stage	Human Health (DALY)	Ecosystem Quality (PDF / m² / yr)	Human Health (DALY)	Ecosystem Quality (PDF / m² / yr)
Production	2.47×10^{-4}	34.1	1.09×10^{-5}	0.798
Transport	5.96×10^{-8}	0.008	3.63×10^{-8}	0.004
Application	2.21×10^{-5}	25.0	2.26×10^{-5}	25.8
Total	2.69×10^{-4}	59.1	3.36×10^{-5}	26.6
Percent Reduction from Imidacloprid			87%	45%

Table 5: Life cycle endpoint results for Human Health and Ecosystem quality impacts (1 ha basis).

life cycles made in the preceding sections about individual life cycle stages and the important factors within each stage are still true in this alternative LCA scenario, however, such as the importance of individual ingredients in each pesticide production stage, the minor contribution of pesticide transport, and the importance of the tractor usage in comparison to effects due to emissions of pesticide onto the landscape in contributing to the overall life cycle impacts calculated here.

Conclusion

This study represents an illustration of a method for comparing environmental impacts of pesticides across their life cycles of production, transportation, and application. This LCA method has been applied to 2 neonicotinoid pesticides, using the best available data, to compare the environmental impacts of each life cycle and offer guidance on potential areas for improvement, both for future studies and the ultimate pesticide life cycle designs. In this study, Thiamethoxam appears to offer considerable advantages over the first generation Imidacloprid pesticide, on the basis of Human Health and Ecosystem Quality. Production data for commercial products made by private industry is always difficult to acquire for the purposes of public LCA studies, but due to the importance of the production stage in this LCA, efforts should be made to continually improve the understanding of how these pesticides are made on a commercial scale, in order to reduce the uncertainly associated with modeling this stage. Once the commercial processes are better understood, more guidance can be offered in terms of how best to reduce environmental impacts of concern through eliminating certain synthesis routes, reducing use of impactful chemicals and solvents, and other approaches. The life cycles of these pesticides are likely to involve global supply chains that link production and consumption locations, but initial efforts at modeling life cycles that involve significant transportation steps reveal that these transport modes appear to influence the overall life cycle in a minimal fashion. Pesticide application should be performed as efficiently as possible, and the ability to use less pesticide when protecting a given quantity of agricultural land can have positive repercussions throughout the supply chain, as less material needs to be produced, transported, and applied to yield the same impact. Although the neonicotinoid pesticides under study here have come under considerable scrutiny for their potential impacts on bee populations, the initial attempts here to model what the Human Health and Ecosystem Quality impacts would be for pesticide application seem to indicate that the impacts associated with operating the tractor have a larger ultimate impact than the actual emissions of the pesticide itself onto the land. This toxicity modeling was performed by relating the available common toxicity metrics for the neonicotinoid pesticide and a third proxy pesticide in the SimaPro LCA modeling platform. This approach has been described in detail, but additional toxicity data for the neonicotinoid pesticides should ultimately be verified by multiple research teams and made publicly available within life cycle inventory databases and modeling platforms to facilitate the study of these environmental impacts. In addition to focusing on the toxic impact of the pesticides as they are released in the environment, this initial study suggests that the environmental impacts associated with tractor usage during pesticide application are actually a larger source of environmental harm in multiple impact categories, and this should be one large focus of the goal of achieving life-cycle reductions in the impact of pesticide use in agricultural systems.

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