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Environmental cost and impacts of chemicals used in agriculture: An integration of emergy and Life Cycle Assessment

Yanfeng Lyu [a], Marco Raugei [b], Xiaohong Zhang [a], Salvatore Mellino [c], Sergio Ulgiati [c,d,*]

[a] College of Environmental Sciences, Sichuan Agricultural University-Chengdu Campus, Chengdu, Sichuan, 611130, PR China
[b] Faculty of Technology, Design and Environment, Oxford Brookes University, Wheatley Campus, Wheatley, Oxford, UK
[c] Department of Science and Technology, Parthenope University of Naples, Centro Direzionale, Isola C4, 80143, Napoli, Italy
[d] School of Environment, Beijing Normal University, Beijing, 100085, PR China

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ABSTRACT

Modern intensive agriculture worldwide is generating increasing environmental pressure, which prevents its sustainable development. A number of agricultural sustainability assessment approaches and methodological frameworks have been developed by research worldwide to assess the environmental costs and impacts of resources used in agricultural production. A joint use of Life Cycle Assessment (LCA, to assess a process' performance and environmental impacts) and Emergy Accounting (EMA, to estimate environmental support to resource generation and provision) is proposed in this study. The goal is not only to ascertain the environmental 'cost' of production of selected chemical resources used in agricultural processes, but also to develop a reliable calculation procedure capable to integrate the two approaches (LCA and EMA), while considering their different allocation algebra and space-time scales of application. Specifically, the UEVs of glyphosate and urea, which are respectively the most used herbicide and nitrogen fertilizer used in worldwide agriculture, are calculated, yielding values of 2.47E+13 sej/kg and 7.07E+12 sej/kg, respectively. In order to do so, UEVs of intermediate process chemicals such as ammonia, acetic anhydride, chlorine gas, formaldehyde, phosphorous chloride, and sodium hydroxide have also been calculated or updated, thus providing at the same time a procedure and a set of values potentially useful for future studies. The LCA impacts of agro-chemicals in China are compared to worldwide averages from the Ecoinvent database, and the UEVs for several chemicals are also compared to previous estimates from published emergy literature.

1. Introduction

Modern agriculture requires a variety of external inputs to maintain production and profits. In particular, the use of chemical fertilizers and pesticides can enhance food production, while reducing crop pests and diseases effectively, to meet the increasing food demand associated to population growth [1,2]. At the same time, the excessive use of large amounts of chemical fertilizers and pesticides generates a series of environmental problems [3,4], such as greenhouse gas emissions [5], water eutrophication [6], soil acidification [7], biological diversity reduction [8], toxicity all over the food chain, and ground water contamination [9]. The high shares of purchased non-renewable resources affects the economic sustainability of chemicals use in agriculture [10], while at the same time the environmental hazards caused by the production of often toxic chemicals can no longer be ignored, to prevent them from becoming an overwhelming threat in the overall resource and environmental balance of agricultural activities. To sum up, agricultural production is currently confronted with the great challenge of feeding a growing population with limited resources while curbing the negative impacts on environmental integrity. Sustainability evaluations may help decision makers and business operators make informed choices on environmentally friendly regulatory measures in production processes. This also applies to agricultural operators, whose activity occurs at the interface of society and nature, where photosynthesis provides food, energy and ecosystem services. Agricultural sustainability assessments characterized by scientifically sound methodological frameworks and well-established and comprehensive methods such as Life Cycle Assessment (LCA) and Emergy Accounting (EMA) are much needed in support of environmental and economic sustainability.

* Corresponding author. Department of Science and Technology, Parthenope University of Naples, Centro Direzionale, Isola C4, 80143, Napoli, Italy.
E-mail address: sergio.ulgiati@uniparthenope.it (S. Ulgiati).

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LCA considers each analyzed process in its relation to the surrounding environment acting as a source and a sink, and relies on inventory databases and several impact assessment methods to develop a few indicators related to impact categories such as global warming, acidification, eutrophication, toxicity, etc. In a like manner, in EMA, resource inflows are associated to characterization factors named Unit Emergy Values (UEVs), which express the demand for environmental support per resource unit at larger spatial and time scales (i.e. the work done by the biosphere to generate a given resource or product), and which can be used to evaluate and compare items on a common basis [11]. UEVs are also important parameters to evaluate the 'environmental efficiency' of the production process, i.e., to what extent the environmental support for resource generation translates into the final product or service, whereby a lower UEV suggests a higher resource use efficiency [12].

Non-renewable inputs have been reported to contribute 60%–80% of the total emergy value of agricultural products, and the emergy of chemicals such as fertilizers and pesticides are reported to account from 25% up to 97% of all non-renewable inputs [13–16]. The glyphosate herbicide is widely used to eliminate unwanted weed species in a wide range of application areas. In 2014, farmers sprayed more than 826 million kilograms of glyphosate with nearly 0.53 kg/ha on all cropland worldwide, making it is the most extensively applied pesticide worldwide [17]. At the same time, nearly 60% of global nitrogen fertilizer use is in the form of urea [18].

In spite of such massive use, a UEV for glyphosate has not yet been calculated in the emergy literature, while the UEV of urea has not been updated since 2002 [19,20]. These two chemicals were therefore selected as case studies in this research.

Therefore, in this work, a framework and a calculation procedure are provided as a step ahead towards further integration of EMA and LCA. Such a procedure will therefore contribute several results:

(1) Highlighting the different LCA impacts, if any, of investigated World average and China–based chemical processes;
(2) providing updated values of the UEVs of glyphosate, urea and other intermediate chemicals;
(3) shedding new light on the geographic variability of environmental accounting (EMA) results; (4) suggesting a (still preliminary) standard method for UEV calculation through LCA/EMA integration.

2. Methods

While LCA is a widely known approach, EMA knowledge is shared by a smaller area of researchers. Therefore, Section 2.1 provides a more in-depth description of the EMA method, while Section 2.2 only discusses the most fundamental characteristics of LCA. Section 2.3 then details how the integration between the two methods is achieved in the present study, as a major step for further improvement.

2.1. Emergy accounting (EMA)

The EMA method was introduced by H.T. Odum in the 1970s, following the worldwide increasing interest in the energy-environment nexus and the embodied energy accounting in the final products [11, 21–23].

In order to express the "natural work embodiment" within each biosphere component, Odum [11] developed the idea of expressing every resource flow in units of so-called emergy (spelled with an M). Emergy (initially intended as "embodied energy") was defined as the amount of available energy (exergy) directly or indirectly required to generate a product or service, expressed in one form of energy (generally solar, with units of solar emergy joule, sej) to ease comparison.

The total emergy U is calculated as the sum of the energy or mass content E_k of each input multiplied by the corresponding UEV_k, according to Eqn. (1a).

$$U = \sum E_k \times UEV_k \tag{1a}$$

where U is the total emergy expressed as sej, E_k is the *k-th* available energy (exergy) flow of matter and energy provided to the system, UEV_k is the unit emergy value characterizing the *k-th* inflow, i.e., the emergy invested to generate one unit of that inflow (Eqn. (2), below). Flows E_k can be renewable (total of which indicated as R), nonrenewable (N), imported or purchased from outside (F), or direct and indirect labor (respectively Labor & Services, L&S; [24], so that Eqn. (1a) can also be written as,

$$U = R + N + F + (L\&S) \tag{1b}$$

Since the emergy supporting L&S is country-specific, we will not include L&S in the calculation of UEVs in this study. L&S calculation and meaning can be found in Ulgiati and Brown [24].

All emergy values refer to a Geobiosphere Emergy Baseline (GEB), representing the total annual emergy driving the biosphere (solar, gravitational, geothermal, as in Figure S1 of Supplementary Material), the value of which affects, of course, all the calculated UEVs [25]. Since the first years of emergy theory development, GEB has experienced several revisions due to the different calculation methods by researchers [11,26–29]. In this study, the most recent GEB estimate is referred to, i.e. 12.0 E+24 seJ/yr [29], for calculation of all other UEVs and indicators. All the UEVs originally calculated with reference to previous emergy baselines have been updated to the most recent GEB. As mentioned above, the amount of emergy needed to generate one unit of product or service is defined as UEV and expressed in terms of sej/unit. When the output is expressed in units of exergy (J), the UEV can be named transformity (sej/J); if a unit of currency is used (e.g. $, €, ¥) the term emergy-to-money ratio (sej/currency) is preferred. In EMA, UEV is a core concept and it is fundamental to the emergy evaluation. UEVs always refer to the space and time scales of the entire biosphere and, consequently, may sometimes be characterized by large uncertainty [30, 31]. In this study, UEVs are calculated by dividing the sum of all emergy inflows required for producing an output by the units of product output, according to the emergy algebra (see Section 2.4.3 on how to prevent double counting). The UEV of one product can therefore be calculated according to Eqn. (2):

$$UEV_p = U / Y_p \tag{2}$$

Where: UEV_p is the UEV of the final product p, U is the total emergy required in the process, including renewable and nonrenewable energy and material resources, and Y_p is the yield of the process, i.e. the available energy (exergy) or mass content of the product.

Other indicators can be calculated, among which, for example, the percentage of renewable emergy in relation to the total emergy U (R/U, named %REN), the emergy per unit land and time (named Empower Density, sej $m^{-2} \cdot s^{-1}$), and so on [11].

2.2. Life Cycle Assessment (LCA)

LCA is a well-known assessment tool for the compilation and evaluation of the inputs, outputs and potential environmental impacts of a product system over its entire life cycle, from the acquisition of raw materials, via the generation of the final product(s) to disposal after use [32,33]. The LCA structure foresees four different steps (definition of goal and scope, inventory, impact assessment, interpretation) interacting each other in order to adjust the analysis to the objectives of the analyst, the boundary of the investigated system, the quality of available data, the problems occurring during the investigation, and so on (Supplementary Material, Figure S2). LCA provides indicators related to different environmental impact categories, such as climate change, acidification, land use, stratospheric ozone depletion, resource depletion, human and ecosystem toxicological effects, among others. Among the most crucial LCA calculation procedures, the allocation step cannot be disregarded. Allocation occurs when a process yields two or more products (e.g., grain and straw, electricity and hot water, cheese and whey, etc). The investigator faces the situation of attributing the process inputs and the related impacts to each of the outputs. For the sake of clarity, this is a virtual procedure, where the assumption is made that each output can be produced without also producing the other one, which is not true in almost all the cases. This means that grain and straw, being produced together, require for production the entire amount of input resources, and so do electricity and heat and many other co–products. For this reason, LCA rules generally discourage allocation procedures, suggesting the so–called "system expansion" [34–36]. The real challenge on the LCA side, however, is that most LCA practitioners apply several allocation procedures (causal, physical, economic) and the LCA Ecoinvent database applies a default economic allocation [37]. In the following Section 2.4.1 a procedure to deal with these allocation procedures is shown.

All the LCA analyses in the present study have been carried out using the OpenLCA 1.10 software package [38] with the Ecoinvent 3.1 database [37] and ReCiPe Midpoint (H) assessment method [39], where H stands for Hierarchical and refers to the way impacts to the different biosphere components are allocated. The 18 midpoint categories resulting from the ReCiPe 2016 Midpoint (H) method application are listed in Table 1. Processes in Ecoinvent are labelled according to the geographical area where data come from (e.g. IT, Italy; CN, China; RER, Europe; etc.). In Ecoinvent 3.1 (year 2013) the acronym GLO (Global) indicates activities which are "*considered to be an average valid for all countries in the world*". Instead, RoW (Rest of the World) indicates average processes at World level excluding countries individually evaluated in the database. Since these countries are only a very small number for each process, RoW and GLO are in most cases very similar. In Ecoinvent 3.2 (released in the year 2015) "*the RoW is generated as an exact copy of the GLO dataset with uncertainty adjusted … The newly generated RoW is then linked with activities of an adequate geographies creating RoW specific supply chain*".[1] In our Tables and calculations for intermediate and final chemicals we finally modified these Ecoinvent RoW data on the basis of existing and identifiable differences between China and World averages (e.g. electricity mix, heat generation mainly from coal combustion, specific mineral processing technologies, water use, etc.), in order to create reliable China inventories for comparison.

Table 1
Impact categories investigated within the ReCiPe 2016 Midpoint (H) method.

Name	Unit
Freshwater ecotoxicity	kg 1,4-DCB
Ozone formation, Human health	kg NO_x eq
Marine eutrophication	kg N eq
Water consumption	m^3
Stratospheric ozone depletion	kg CFC11 eq
Freshwater eutrophication	kg P eq
Terrestrial acidification	kg SO_2 eq
Human carcinogenic toxicity	kg 1,4-DCB
Terrestrial ecotoxicity	kg 1,4-DCB
Global warming	kg CO_2 eq
Human non-carcinogenic toxicity	kg 1,4-DCB
Fossil resource scarcity	kg oil eq
Fine particulate matter formation	kg PM2.5 eq
Ozone formation, Terrestrial ecosystems	kg NO_x eq
Land use	m^2a crop eq
Marine ecotoxicity	kg 1,4-DCB
Ionizing radiation	kBq Co-60 eq
Mineral resource scarcity	kg Cu eq

2.3. Previous methodological LCA and EMA integration efforts

Increased efforts are being implemented in order to generate a synergistic integration between the very extensive databases and standardized calculation procedures supporting the LCA method and the broad and comprehensive conceptual framework of the EMA approach. Several authors have expressed the urgent need to develop an integrated framework and software [40–43], but the different specific goals, allocation procedures, spatial and time scales have been, so far, crucial barriers for this to happen. According to Bakshi [44] the analysis of both ecological and industrial processes is required to make ecologically conscious decisions in engineering processes; an Emergy-based LCA is proposed to combine the benefits of both methods. In a second article [45], the same author proposed the exergy analysis method to provide a holistic measure of the impact of emissions (in terms of exergy loss). Marvuglia et al. [41] developed SCALE (Software for CALculating Emergy), a software based on life cycle inventories capable of calculating emergy performance indicators while rigorously applying the emergy algebra rules. Raugei et al. [43] claimed that EMA and LCA share similarities and that EMA may represent a valuable addition to LCA, warning however that the two methods present very different characteristics in terms of goals, scope, definitions and calculation procedures and that their integration requires careful considerations. Bala Gala et al. [46] argued that the peculiar emergy algebra might represent the major barrier for the integration between LCA and EMA. Marvuglia et al. [40] highlighted once again that EMA could benefit from the use of existing LCA databases since it has often suffered from simplified accounting models as well as incomplete data inventories [47]. Recently, Santagata et al. [48] proposed a methodological procedure based on the sequential and integrated application of LCA and EMA, called LEAF (LCA & EMA Applied Framework). The sequential application of LCA and EMA provided insights from the donor side (EMA) and from the user side (LCA) points of view, allowing a deeper understanding of the analyzed processes and of optimization scenarios.

From the literature review it appears that the integration of EMA and LCA may represent an added value when assessing the environmental performance of systems by providing additional indicators that quantify the environmental support required. It also emerges that the best solution would be the implementation of the EMA method within the main LCA workstream.

The joint utilization of LCA and EMA had already been applied to a range of case studies, among which solid waste management [49], electricity generation [31], waste and by-product reutilization [50,51], and industrial processes [52,53]. The main benefits of a joint application of the two methods can be summarized by the following aspects: (1) combining a donor-side (EMA) with a user-side (LCA) assessment of environmental impacts [49], and (2) expanding the spatial and time scales of process-based LCA to include EMA's consideration of the environmental work needed to replace what is consumed [43].

Specifically, in the past two decades, production processes of chemicals have experienced significant technological innovations, but the estimation of the UEVs of chemicals in the literature has not kept up with such innovations, with the result that many reported UEVs are now obsolete. In fact, only very few emergy studies about minerals and chemicals, in the earth crust [54] or in production processes [52,53], have been published until now. Also, EMA has sometimes been the object of criticism regarding its small database, a not fully clear methodological framework [55,56], and low inventory accuracy or lack of standardization of the evaluating procedure [57]. This has recently led to an increased standardization effort [25,29,31,48,58]. A major difficulty, when attempting to calculate more accurate and up to date UEVs, lies in data acquisition. It is clear that more detailed process inventories and comprehensive models are needed for UEV calculations. Actually, emergy practitioners have experienced a hard time in generating

[1] (https://www.ecoinvent.org/support/faqs/methodology-of-ecoinvent-3/what-do-the-shortcuts-such-as-ch-rer-row-and-glo-mean.html).

inventories for emergy calculation of many processes. The use of well-established LCA databases such as Ecoinvent and others may thus provide valuable data in support of UEV calculations, but only researchers who are experts of both emergy and LCA can so do.

2.4. Calculating UEVs from LCAs of the investigated agro–chemicals

In the present work we track back the Ecoinvent LCA inventories for the investigated chemicals, in order to recover the original input resources of the process before economic allocation takes place, i.e., the original inflows supporting the real process with two or more co–products, instead of the modified process with one product only and its recalculated, allocated inflows. In so doing we create the premises for the calculation of the UEV of each output, as a compromise of both the EMA algebra (no allocation, Section 2.4.3) and the LCA standard rules (system's expansion for no allocation or allocation according to a well identified physical property).

2.4.1. Target products

As mentioned above, two chemicals of general interest for agriculture were selected as case studies: glyphosate and urea. Glyphosate is the preferred herbicide in the agro-industry, making it the largest globally traded agrochemical [17]. Urea is widely used in fertilizers as a source of nitrogen (N) and it is an important raw material for the chemical industry. In the industry, glyphosate is a synthetic phosphonate compound [59] and urea is produced from synthetic ammonia and carbon dioxide. The urea production process is relatively simple, whereas the production process for glyphosate is more complex.

Specifically, the innovation in our work is to go back to the not–allocated inventories and convert them into not–allocated emergy values. The emergy procedure performed without allocating the driving emergy to coproducts [11,58] is very similar to the standards of LCA theory ("avoid allocation when possible"), although this is most often disregarded because allocation according to monetary values is very easy and can be performed using statistical economic yearbooks, easy to find for every kind of commodity.

Assuming an intermediate or final process in the whole supply chain only has one output, there is no allocation problem and the inventory used for LCA impact indicators can be also used to calculate the UEV of the resulting intermediate product, by simply applying the Eqns. (1) and (2).

Instead, in the presence of two or more co–products, the problem is that there is no process in Ecoinvent showing both as co–products of the same process. Each of the two (or more) co– products is shown in the database as an individual product of a process where all the inflows are set as proportional to the percentage fraction of monetary value (or, less frequently, energy or mass value) that this product is, compared to total production (Eqns. (3) and (4)):

$$f_i = F_i \times \%T_i \tag{3}$$

allocated inventories
or vice versa

$$F_i = f_i / \%T_i \tag{4}$$

not allocated inventories.where F_i is the *i–th* flow of the not–allocated inventory; f_i is the flow associated to the co–product that provides a given % of total economic or energy or mass value; $\%T_i$ is the percentage that this co–product is of total process output product. Eqns. (3) and (4) apply to both co–products and can be extended to more than two co–products, if needed. Because of Eqn. (3), the Ecoinvent database provides an inventory tailored to one unit of each co–product, which is, of course, only a "virtual process", because, generally, a process that can provide only one of the two co–products, separately, does not exist. Eqn. (4) helps recalculate the total amounts of each inflow F_i from which the two co–products originate simultaneously in the real process. As a consequence of proportional input flows, also the calculated impact indicators will be proportional to the amounts of inflows. This is a most common allocation practice in LCA.

Once the "not–allocated" inventories are calculated for the worldwide average based on Ecoinvent data and Eqn. (4), LCA inventories were also adjusted for glyphosate and urea as well as for all the intermediate chemicals and energy flows occurring along their supply chains in China. In order to do so, China-based production inflows of electricity, heat, fuel for transport services, selected minerals for machinery and infrastructures were also considered for the China–based inventories (e.g.: magnesium, steel, transport infrastructures, [60–62]), although sometimes they provided a negligible contribution to processes, due to the amortization over time. After accounting for the main differences between World and China production processes, the China-based inventories were used as the calculation basis for new or updated UEVs applicable to China' agriculture.

2.4.2. Production flows

Both production processes (glyphosate and urea) are shown in Fig. 1 as systemic diagram and Figure S3 in the Supplementary Material as conventional flow-chart. Compared to conventional flow charts, systemic diagrams, developed by Odum [63] and Brown [64], help understand mutual relations and role of system's components as well as resource inflows and outflows. Resource inflows are: underground minerals, fossil fuels and underground water, while machinery, land used, solar radiation and other free environmental inflows are shown as global inputs to the entire system considering their small amounts to all investigated processes. As mentioned above, the input of Labor and Services (L&S) will not be considered in the present work, since LCA does not include them in its databases. Interested readers can extract all needed information from Ulgiati and Brown [24]. Product flows are: glyphosate, urea, intermediate chemicals, electricity and heat generated or used throughout the manufacturing processes. Outflows are: low temperature heat and chemical emissions, globally indicated by the so–called "sink symbol". All sub–processes in Fig. 1 are described in detail in Supplementary Materials (Tables S1 to S26). Among them, Tables S3-Table S12 and Table S17 are referenced from Ref. [65], as basic UEVs for sustainability evaluation of a rice production system.

Fig. 1 can be understood starting from inflows of minerals and fossil fuels. Fossil fuels (mainly coal) are used for cogeneration of heat and power (CHP) which supports intermediate and final chemicals production. Power is an input to all downstream processes, while heat only supports the following processes: heavy fuel oil production from crude oil (Table S6, in Supplementary Material), acetic anhydride production from acetic acid (Table S13), acetic acid production from methanol (Table S14), methanol production from natural gas (Table S16), soda ash production from lime and NaCl (Table S19), calcium chloride production from lime and NaCl (Table S20), lime production from $CaCO_3$ (Table S21), sodium chloride powder from NaCl in ground (Table S26). Sodium chloride, Calcium carbonate and phosphatic rock are also inputs from underground mainly to support Solvay and Chloralkali processes leading to glyphosate. Some crude oil and natural gas are also used respectively for heavy fuel oil and methanol production, to feed the entire series of processes leading to formaldehyde and acetic anhydride and then to glyphosate. Finally, natural gas is the main inflow for ammonia production and then urea (the latter also being an input to glyphosate production). Each sub–process is indicated by a rectangle containing an interaction arrow. The name of the sub–process product is indicated within the arrow itself. Only in three cases (Chloralkali, Solvay and CHP) sub–processes generate co–products. The names of co-products are therefore written on the flows exiting from each sub–process, while the names of these industrial sub–processes are indicated within the rectangle. The interaction arrows are used when inflows of different nature (e.g., electricity and minerals) converge to generate a higher quality product.

As mentioned in previous sections, in the Ecoinvent database under

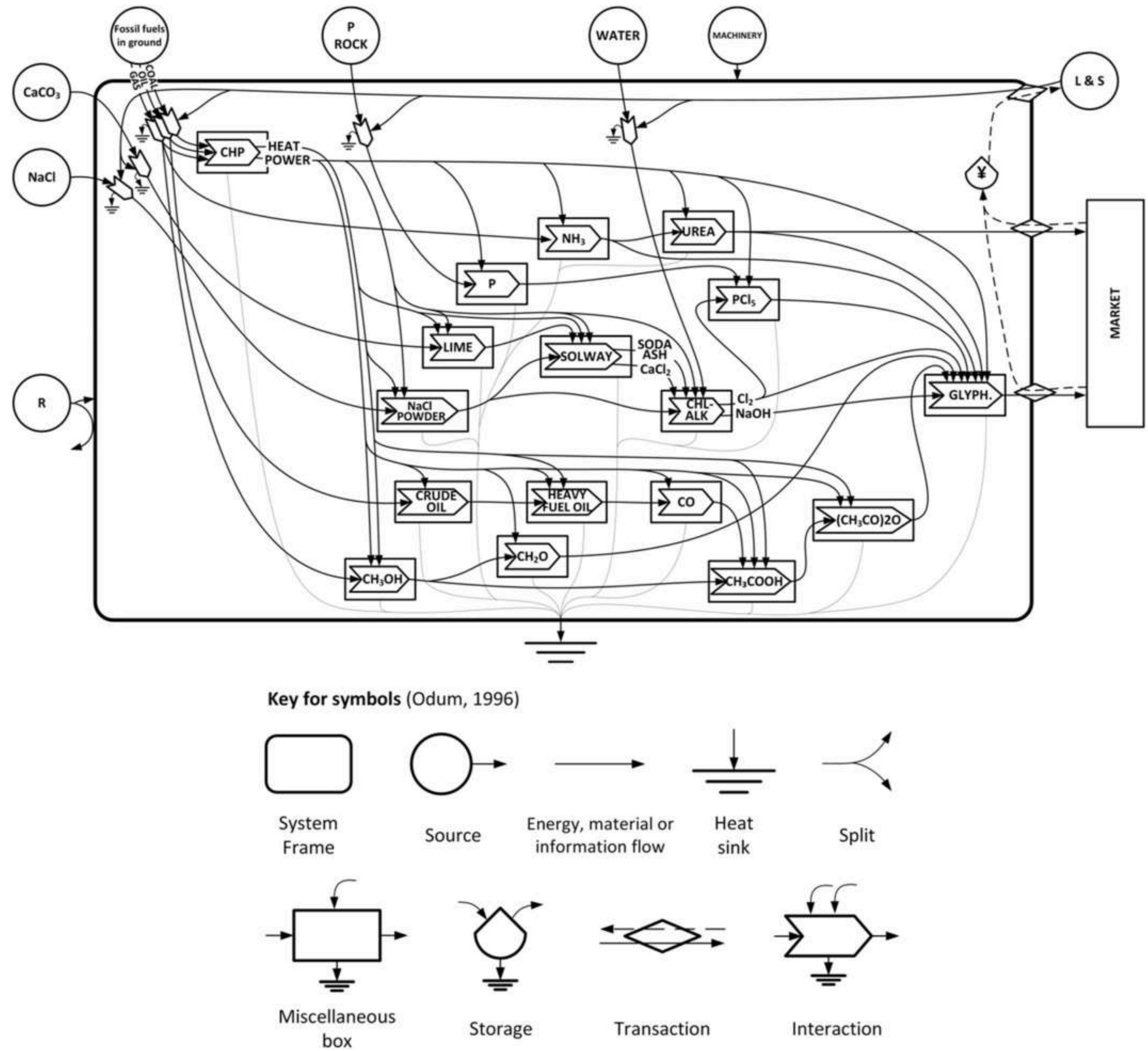

Fig. 1. Material and energy flows for the production of glyphosate and urea (courtesy Remo Santagata).

default allocation rules, only a fraction of the input flows is virtually assigned to the investigated output flow through allocation methods, under the implicit (and incorrect) assumption that the individual co-product can be generated based on a smaller fraction of input resources. However, avoiding allocation is recommended in LCA, whenever possible, reverting instead to a system expansion approach [34–36]. As discussed later on in Section 2.4.3, EMA never allocates the total input emergy U to co-products [11], while instead the total input emergy is assigned to each one of the product flows. Misunderstanding of this emergy algebra rule led several energy and exergy analysts to (incorrectly) criticize EMA for not fulfilling the energy conservation law.

2.4.3. Calculation steps from LCA to EMA, via emergy algebra-adjusted ecoinvent database

The EMA algebraic rules (so-called "memory algebra"), to be followed when combining input and output flows in a network of processes [11,66], can be summarized as follows:

1) when only one product is obtained from a process (i.e., a process with only one output), all source-emergy is assigned to it;
2) when a flow (of emergy) splits, the total emergy also splits accordingly, based on the exergy or energy or mass in each pathway;
3) when two or more co-products are generated in a process, all independent input emergy is assigned to each co-product (no allocation);
4) emergy cannot be counted twice within a system:
   - (4.1) emergy in feedbacks cannot be double counted;
   - (4.2) co-products, when reunited, cannot be summed and only the emergy of the largest co-product flow is accounted for.

The calculation flow is shown in Fig. 2 and a detailed calculation procedure is developed as follows.

(1) According to production characteristics of the analyzed systems (urea and glyphosate production), the corresponding processes in the Ecoinvent database were identified. As mentioned in Section 2.2, the respective Ecoinvent processes were adjusted to the

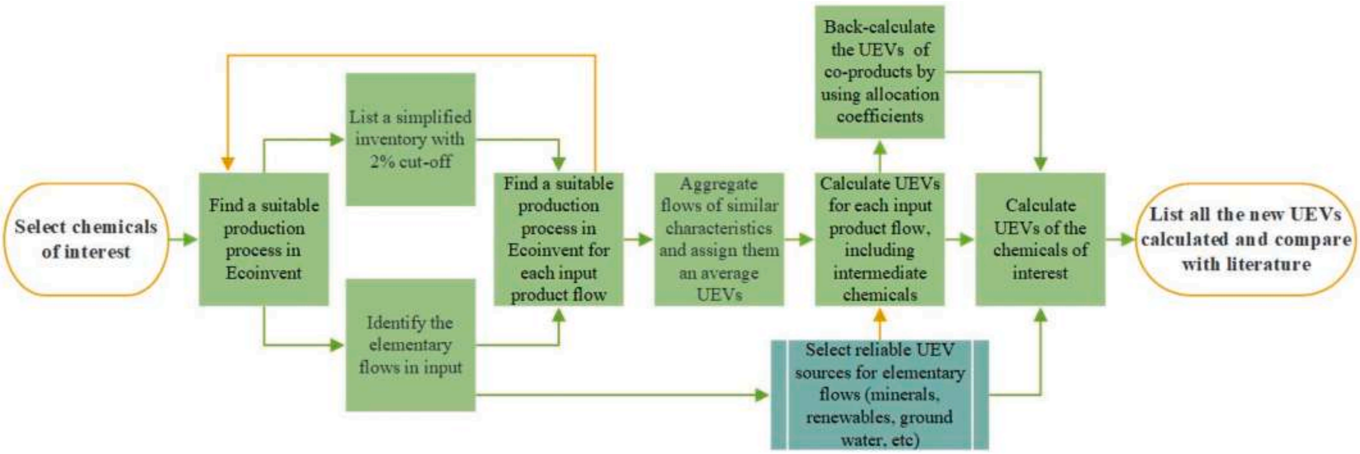

Fig. 2. Calculation flow of integrated LCA and emergy analysis [65].

Chinese reality by using the location-appropriate models for electricity generation, transportation, etc.

(2) Simplified inventories with 2% mass or energy cut-off were generated for the investigated Chinese production chains. The emergy method does not consider output flows, because they are generated by the same driving resources already accounted for in input to generate the products. Treatment of output flows for their disposal or abatement could be included, but the LCA Ecoinvent database shows this treatment input to be very small and therefore negligible. In some cases, energy inputs for such a treatment are already included within energy inputs driving the process in the Ecoinvent database. As mentioned above, the 2% cut–off also excludes inputs of minerals and metals for vehicles and infrastructures, whose amortization over many years makes their annual contribution negligible.

(3) UEVs of basic inflows (named elementary flows in LCA) were used to generate in sequence all the other UEVs, according to the LCA inventories, adjusted - as explained above - to fit the process characteristics in China. Heat and electricity are co-products from co-generative coal and natural gas power plants; soda ash and calcium chloride are co-products from a Solvay process; chlorine gas and sodium hydroxide are co-products from a chloralkali process. The existence of co-products makes the calculation more difficult due to the already mentioned "memory algebra" of the emergy approach, conflicting with the allocation algebra most often used in LCA. In the three processes above, characterized by co-products, the LCA algebra applied in the Ecoinvent database allocates inflows according to the economic value of the co-produced flows. The procedure described in Section 2.4.1 and Eqns. (3) and (4) were thus used to trace back the total input flows driving the process and back-calculate the related UEVs in accordance with the emergy algebra described at the beginning of this Section 2.4.3. Then, the not–allocated input flows are used for co–products UEV calculation. For instance, Table S19 and Table S20 in the Supplementary Material show the production of soda ash and calcium chloride, respectively. Both products are from the multioutput process "Solvay process". Allocation to the two co-products in Ecoinvent is done by using market prices, resulting in 33% to soda and 67% to calcium chloride. These allocation fractions were used to back–calculate the total emergy driving the Solvay process and, therefore, each of the output flows according to the EMA procedure. In so doing, UEVs according to the emergy algebra as well as the LCA system expansion concept were calculated. The not–allocated total emergy and UEV values were then carefully used as an input to downstream processes, taking care of avoiding double counting when co-product flows reunite.

(4) Co-product flows re-uniting into a downstream process after a chain of intermediate steps were carefully checked in order to identify the one carrying the largest emergy and only account for this latter in the total emergy of the downstream product.

(5) The resulting UEVs were then compared with selected UEVs from literature, in order to assess the difference, if any, and confirm the advantages of EMA and LCA integration, in that more reliable EMA results are made possible.

(6) UEVs of basic inflows of minerals, raw fossil fuels and water are mainly derived from previous research by the same authors, as well as from previously published papers and databases [25,29,54,58,67].

(7) UEVs of energy product flows (electricity, heat, refined fuels) were calculated based on the raw materials used and the inventory information in the Ecoinvent database. The UEV of electricity generated by the Chinese grid as a whole was calculated by applying weighting coefficients to all technologies comprising the grid mix, based on the amounts of electricity produced in 2018 (Supplementary Material, Table S3–S8).

(8) Emergy of renewable inflows to the production processes is generally very small compared to nonrenewable inflows, due to the small portion of land involved. The total renewable emergy was calculated based on land occupation associated to the corresponding process, following the calculation procedure described in Brown and Ulgiati [58]. Land occupation is an impact category from the LCA impact assessment method ReCiPe 2016 Midpoint (H) in Ecoinvent. However, considering the very small percentage of the calculated renewable resources compared to the total emergy of the process, renewable flows ended up being irrelevant for the goal of this study and was disregarded in the majority of Tables in Supplementary Materials, due to the abovementioned 2% cut–off choice.

3. Results

In this section, the LCIA results of the investigated Chinese final products (glyphosate and urea) production chain are shown and compared with those calculated using the respective global Ecoinvent database values (Figs. 3 and 4). Further, LCA-based UEVs of glyphosate and urea are also shown (with detailed calculations in the Supplementary Material). Several calculated UEVs are also compared with corresponding UEVs in previously published papers. Calculated UEVs of intermediate chemical products are shown in the Supplementary Material.

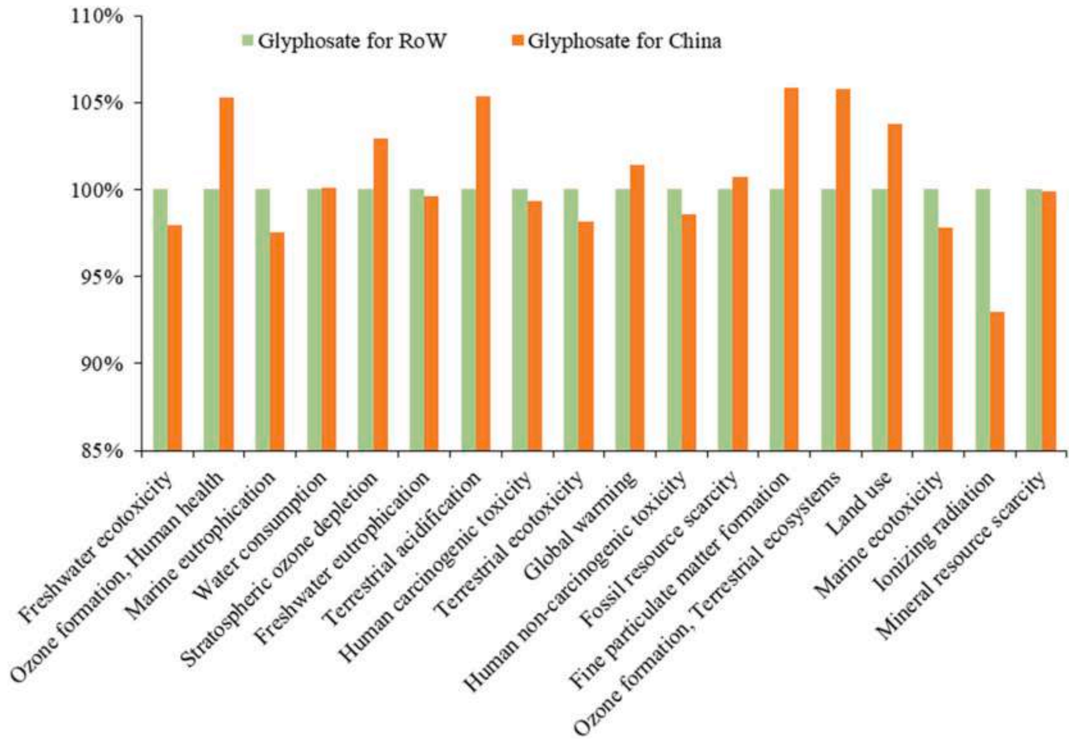

Fig. 3. Comparison of the two scenarios for 1 kg of glyphosate: glyphosate for RoW and glyphosate for China (ReCiPe Midpoint (H) results for impact categories).

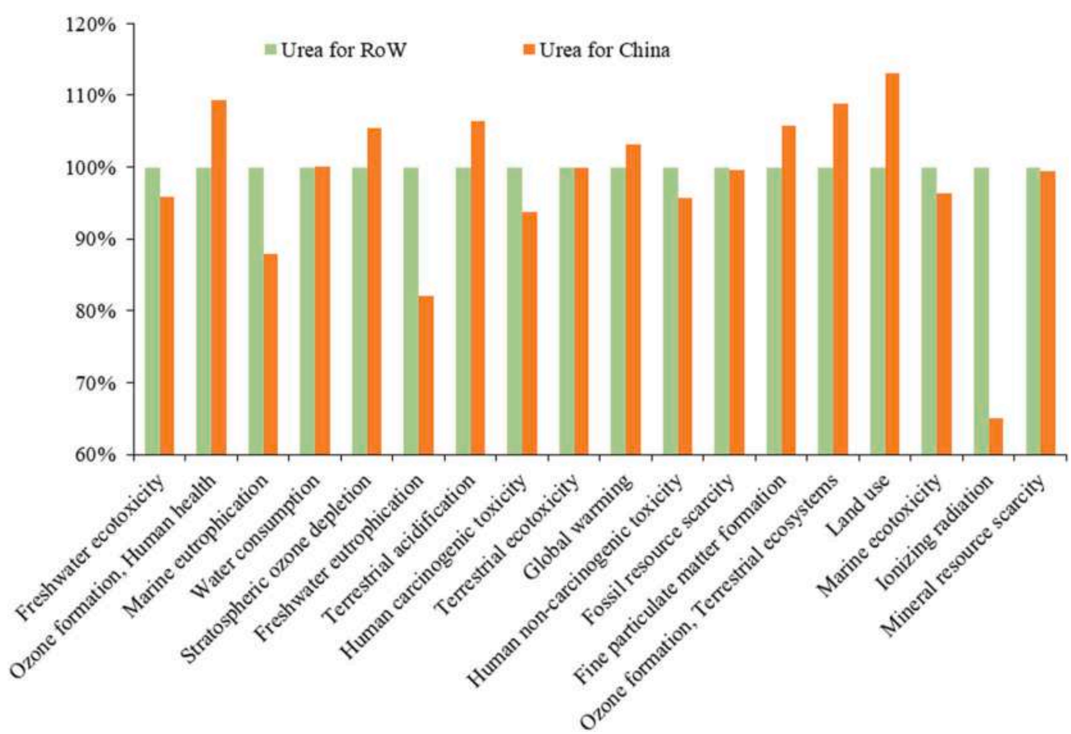

Fig. 4. Comparison of the two scenarios for 1 kg of urea: urea for RoW and urea for China (ReCiPe Midpoint (H) results for the impact categories).

3.1. UEV of glyphosate production in China

As shown in Table 2, the local renewable resource flows were also considered, although they contribute less than 0.05% to the total emergy of glyphosate industrial production. All the imported inputs and transportation costs were also considered. The resulting UEV of glyphosate is 2.47E+13 sej/kg, with acetic anhydride (Table S13, in Supplementary Material) contributing the most (30%), followed by phosphorous chloride (Table S23, 27%), formaldehyde (Table S22, 16%), sodium hydroxide (Table S25, 15%) and electricity (Table S8, 5%).

3.2. UEV of urea production in China

The calculated UEV of urea is 7.07E+12 sej/kg (Table 3), i.e., smaller

Table 2
UEV calculation of glyphosate.

Flows (LCA Ecoinvent v3.1)	Amount	Unit	UEV (sej/unit)	Emergy
Local renewable resources				
Primary emergy sources				
Sunlight	3.23E+08	J	1[a]	3.23E+08
Earth cycle	5.03E+04	J	4900[a]	2.46E+08
Sum of primary emergy sources				*5.70E+08*
Secondary and tertiary sources				
Wind	9.76E-03	J	800[a]	7.81E+00
Rain, chemical potential energy	3.10E+05	J	7000[a]	2.17E+09
Runoff, chemical potential energy	7.76E+04	J	2.13E+04[a]	1.65E+09
Runoff, geopotential energy	8.22E+03	J	1.28E+04[a]	1.06E+08
Largest of 2nd and 3rd sources				*2.17E+09*
Imported inputs				
Acetic anhydride	6.35E-01	kg	1.18E+13[c]	7.47E+12
Ammonia, liquid	1.11E-01	kg	4.54E+12[c]	5.06E+11
Chlorine, gaseous	5.55E-01	kg	3.58E+11[c]	1.98E+12[d]
Electricity, medium voltage	4.32E+06	J	2.85E+05[c]	1.23E+12[e]
Formaldehyde	4.14E-01	kg	9.37E+12[c]	3.88E+12
Heat, district or industrial, natural gas	7.48E+00	MJ	1.33E+11[c]	9.98E+11
Heat, district or industrial, other than natural gas	4.18E+00	MJ	1.03E+11[c]	4.28E+11[f]
Phosphorous chloride	9.39E-01	kg	7.21E+12[c]	6.77E+12
Sodium hydroxide, without water, in 50% solution state	1.25E+00	kg	2.97E+12[c]	3.71E+12[g]
Water, cooling, unspecified natural origin	1.91E-01	m3	1.00E+11[b]	1.92E+10
Transport, freight train	7.76E-02	t*km	4.17E+10[c]	3.24E+09
Transport, freight lorry	3.13E-01	t*km	2.10E+11[c]	6.58E+10
Transport, light vehicle	9.70E-03	t*km	2.84E+12[c]	2.75E+10
Transport, freight ship	3.68E-01	t*km	1.68E+10[c]	6.18E+09
Output				
Glyphosate	1	kg		
Total emergy of glyphosate				2.47E+13
UEV of glyphosate			2.47E+13	

Note: Amounts of input and output data are from the Ecoinvent database (glyphosate production-RoW), assuming the industrial production follows the same standardized steps worldwide, while the UEVs of each flow refer to their production processes in China, assuming a different emergy cost of production due to specific local resource availability and extraction costs. The computational procedure of renewable resources is performed according to Brown and Ulgiati [58], with the total emergy of local renewable resources being calculated as the largest between the primary emergy sources and the largest among secondary and tertiary sources (namely 2.17E+09 sej) to avoid double counting.
Sunlight: Energy (J) = (area) * (insolation-albedo) = (1.10E-01 m^2) * (3.69E+09 J/m^2-7.61E+08 J/m^2).
Earth cycle: Energy (J) = (area)*(heat flow) * (carnot efficiency) = (1.10E-01 m^2) * (5.30E+06 J/m^2) * 0.09.
Wind: Energy (J) = (area) * (density of air) * (wind velocity) * (drag efficient)^3* (time) = (1.10E-01 m^2) * (1.23 kg/m^3) * (0.52 m/s) * (1.64E-03)^3 * (3.15E+07s).
Rain, chemical potential energy: Energy (J) = (area)*(rainfall)*(transpiration rate %) * (gibbs energy of rain) * (density of water) = (1.10E-01 m2) * (0.7449 m) * (80%) * (4720 J/kg) * (1000 kg/m3).
Runoff, chemical potential energy: Energy (J) = (area)*(rainfall)*(runoff rate %) * (gibbs energy of rain) * (density of water) = (1.10E-01 m^2) * (0.7449 m) * (20%) * (4720 J/kg) * (1000 kg/m^3).
Runoff, geopotential energy: Energy (J) = (area)*(rainfall)*(average elevation) * (runoff rate %) * (density of water) = (1.10E-01 m^2) * (0.7449 m) * (500 m) * (20%) * (1000 kg/m^3).
[a] Parameters referenced from [58].
[b] Data are from [68].
[c] Our Calculations based on Ecoinvent, detailed calculation processes are shown in the Supplementary Material.
[d] and.
[g] are co-products from chloralkali process, see Supplementary Material.
[e] and.
[f] are co-products from electric cogeneration, see Supplementary Material.

Table 3
UEV calculation of urea [65].

Flow (LCA Ecoinvent v3.1)	Amount	Unit	UEV (sej/unit)	Emergy (sej)
Local renewable resources				
Primary emergy sources				
Sunlight	1.65E+07	J	1[a]	1.65E+07
Earth cycle	2.56E+03	J	4900[a]	1.25E+07
Sum of primary emergy sources				*2.90E+07*
Secondary and tertiary sources				
Wind	4.97E-04	J	800[a]	3.97E-01
Rain, chemical potential energy	1.58E+04	J	7000[a]	1.11E+08
Runoff, chemical potential energy	3.95E+03	J	2.13E+04[a]	8.42E+07
Runoff, geopotential energy	4.19E+02	J	1.28E+04[a]	5.38E+06
Largest of 2nd and 3rd sources				*1.11E+08*
Imported inputs				
Ammonia, liquid	1.23E+00	kg	4.54E+12[c]	5.58E+12
Electricity, medium voltage	1.15E+06	J	2.85E+05[c]	3.29E+11
Heat, district or industrial, natural gas	8.05E+00	MJ	1.33E+11[c]	1.07E+12
Water, unspecified natural origin	2.86E-01	m^3	1.00E+11[b]	2.87E+10
Transport, freight train	2.76E-01	t*km	4.17E+10[c]	1.15E+10
Transport, freight lorry	1.49E-01	t*km	2.10E+11[c]	3.12E+10
Transport, freight ship & inland waterways	8.88E-01	t*km	1.68E+10[c]	1.49E+10
Output				
Urea, as N	1	kg		
Total emergy of urea				7.07E+12
UEV of urea, as N			7.07E+12	

Note: Amounts of input and output data are referred to Ecoinvent database (glyphosate production-RoW), while UEVs refer to China production processes. In a like manner as in Table 2, kinetic energy of tide is not included among renewable resources. According to the computation procedure mentioned in the footnote of Table 2, the emergy of local renewable resources is computed as 1.11E+08 sej.
Sunlight: Energy (J) = (area) * (insolation-albedo) = (5.62E-03 m^2) * (3.69E+09 J/m^2-7.61E+08 J/m^2).
Earth cycle: Energy (J) = (area)*(heat flow) * (carnot efficiency) = (5.62E-03 m^2) * (5.30E+06 J/m^2) * 0.09.
Wind: Energy (J) = (area) * (density of air) * (wind velocity) * (drag efficient)^3* (time) = (5.62E-03 m^2) * (1.23 kg/m^3) * (0.52 m/s) * (1.64E-03)^3 * (3.15E+07s).
Rain, chemical potential energy: Energy (J) = (area)*(rainfall)*(transpiration rate %) * (gibbs energy of rain) * (density of water) = (5.62E-03 m^2) * (0.7449 m) * (80%) * (4720 J/kg) * (1000 kg/m^3).
Runoff, chemical potential energy: Energy (J) = (area)*(rainfall)*(runoff rate %) * (gibbs energy of rain) * (density of water) = (5.62E-03 m^2) * (0.7449 m) * (20%) * (4720 J/kg) * (1000 kg/m^3).
Runoff, geopotential energy: Energy (J) = (area)*(rainfall)*(average elevation) * (runoff rate %) * (density of water) = (5.62E-03 m^2) * (0.7449 m) * (500 m) * (20%) * (1000 kg/m^3).
[a] Parameters referenced from [58].
[b] Data are [68].
[c] Our Calculations based on Ecoinvent, see Supplementary Material.

than for glyphosate. Like in the glyphosate calculation (Table 2), local renewable resources contribute less than 0.01% to the total emergy of urea. The largest share of total emergy was liquid ammonia (Table S17, 79%), followed by heat from natural gas (Table S1, 15%) and electricity (Table S8, 5%).

3.3. Results comparison

All the UEVs calculated in this study (most of which in the

Supplementary Material) are shown in Table 4 (with all detailed calculation procedures) and some of them are compared, in Table 4, with UEVs from published literature. The UEV of electricity (weighted average for China in 2018; Table S8) was 30% higher than the UEV of electricity for China in the National Environmental Accounting Database v2.0 (NEAD v2.0) [69]. Electricity from coal (Table S3), the largest share in China, was also 30% higher than the corresponding UEV in the literature [70]. UEV of electricity from natural gas (Table S5) is surprisingly 250% higher than the one calculated by Brown and Ulgiati [71]. UEVs of sodium hydroxide (Table S25) were 13% higher than the number in published paper [52], while UEV of liquid ammonia (Table S17) was 60% and 52% lower than [53,72], respectively. Similarily, UEV of sodium chloride (Table S26) was 70% and 29% lower than the UEVs in Refs. [73,74], respectively. Values of UEVs calculated based on Ecoinvent database in this study were lower than those in published papers also occurred for acetic acid, methanol, chlorine gaseous. Moreover, the UEV for urea (Table 3) was 33% higher than he one in Ref. [19] while 61% lower than the one in Ref. [20]. Similar considerations apply to calculated UEVs of heavy fuel oil and some transportation modalities. Using the LCA database provides a more complete inventory, which may partially justify the higher values. A higher value of calculated UEVs is not generally to be considered a good result, since it means more environmental resource investment for the same amount of output. The difference in the calculated values may also depend on other factors expressing technological differences between China and other nations or areas in selected sectors (just think of the different electricity mix in China compared to the World average).

Finally, attention needs to be paid to the difference between the calculated LCIA indicators for Chinese processes and the values for the corresponding processes in the Ecoinvent database. Results for China and RoW glyphosate are shown in Fig. 3, and for urea in Fig. 4, with RoW percentage set as 100%. Only very few impact categories (mainly for urea) show differences larger that 5%. These Figures point out a small difference in all impact categories (in the range ±5%, approximately compared to RoW data considered as reference). A partial explanation of these results may be that the Chinese manufacturing sector is an important part of World production: China produced around 40% of the world's glyphosate supply, most of which exported [80], 30% of the word's urea supply, 30% of which exported, and large fractions of intermediate chemicals, according to Ref. [81]. The contribution of China to the RoW impacts is therefore so large (both in decreasing some of the impacts and increasing others) that the RoW results are very similar to China-tailored impacts. Consequently, the calculated UEVs, based on foreground RoW-tailored processes and background Chinese data are applicable to future studies related to both situations.

Table 4
UEVs results and selected comparison (all values without L&S).

Items	UEVs		References
	This study	Previous studies	
Electricity (sej/J)	2.85E+05	2.21E+05	[69]
Electricity - coal (sej/J)	2.87E+05	2.24E+05	[70]
Electricity - natural gas (sej/J)	4.25E+05	1.22E+05	[71]
Ammonia, liquid (sej/kg)	4.54E+12	1.14E+13	[53]
		9.39E+12	[72]
Sodium hydroxide (sej/kg)	2.97E+12	2.62E+12	[52]
Sodium chloride, powder (sej/kg)	2.44E+11	8.33E+11	[73]
		3.43E+11	[74]
Urea, N (sej/kg)	7.07E+12	5.33E+12	[19]
		1.83E+13	[20]
Glyphosate (sej/kg)	2.47E+13	–	–
Heavy fuel oil (sej/kg)	6.72E+12	5.26E+12	[75]
Acetic anhydride (sej/kg)	1.18E+13	–	–
Acetic acid (sej/kg)	8.02E+12	2.29E+13	[76]
Methanol (sej/kg)	8.82E+12	9.19E+12	[77]
Carbon monoxide (sej/kg)	6.80E+12	–	–
Chlorine, gaseous (sej/kg)	3.58E+12	5.78E+12	[77]
Calcium chloride (sej/kg)	1.27E+12	–	–
Soda ash (sej/kg)	1.20E+12	–	–
Formaldehyde (sej/kg)	9.37E+12	–	–
Phosphorous chloride (sej/kg)	7.21E+12	–	–
Phosphorus, white, liquid (sej/kg)	1.76E+13	–	–
Heat, natural gas (sej/MJ)	1.33E+11	–	–
Heat, other than natural gas (sej/MJ)	1.03E+11	7.47E+10	[78]
Transportation, lorry (sej/t*km)	2.10E+11	1.84E+11	[62]
Transportation, light commercial vehicle (sej/t*km)	2.84E+12	1.65E+11	[79]
Transportation, rail (sej/t*km)	4.17E+10	8.09E+10	[62]
Transportation, ship (sej/t*km)	1.68E+10	–	–

4. Discussion and conclusions

Results point out the importance of accurate LCA indicators and associated UEVs for full and multidimensional sustainability assessment. The results of this study reveal the need for improvement in resource allocation and calculation method in LCA allocation procedures (to be possibly avoided so that the real process yielding co–products is shown in the Databases) as well as for increased worldwide studies about chemicals for agriculture and food management.

4.1. *The importance of accurate UEVs*

From 2000 to 2015, the amount of pesticides and fertilizers used in China increased by 39% and 45%, respectively [82]. Since 2015, a zero-growth plan for fertilizers and pesticides use by 2020 [83,84] has been advocated in order to achieve an agricultural development characterized by economic efficiency and sustainable development patterns. Compared with 2015, in the year 2018 a non–negligible improvement has been obtained thanks to the reduction of fertilizers and pesticides by 31% and 16% respectively. The reduction of chemicals application will likely generate changes in supply and production. Most farmers rely on glyphosate throughout the entire process of agricultural production, and in particular: (1) utilization before sowing to facilitate reduced tillage, (2) application before harvesting in order to facilitate the use of agricultural machinery, and (3) application after harvesting to reduce weeds growth [85]. The large use of glyphosate as well as urea have led to public and scientific debates about possible ecological and human health impacts during their manufacture, transportation, and application [86].

Table 5
Impact categories of glyphosate and urea of China.

Name	Glyphosate for China	Urea for China	Unit
Freshwater ecotoxicity	0.33359	0.03643	kg 1,4-DCB
Ozone formation, Human health	0.02936	0.00527	kg NOx eq
Marine eutrophication	0.00475	0.00022	kg N eq
Water consumption	0.29308	0.18344	m3
Stratospheric ozone depletion	7.47E-06	1.16E-06	kg CFC11 eq
Freshwater eutrophication	0.01478	0.00023	kg P eq
Terrestrial acidification	0.06443	0.02238	kg SO2 eq
Human carcinogenic toxicity	0.36613	0.03503	kg 1,4-DCB
Terrestrial ecotoxicity	29.91341	12.77723	kg 1,4-DCB
Global warming	11.98478	3.32216	kg CO2 eq
Human non-carcinogenic toxicity	7.22196	0.97165	kg 1,4-DCB
Fossil resource scarcity	3.66442	1.26332	kg oil eq
Fine particulate matter formation	0.02602	0.00716	kg PM2.5 eq
Ozone formation, Terrestrial ecosystems	0.03024	0.00543	kg NOx eq
Land use	0.11463	0.00643	m2a crop eq
Marine ecotoxicity	0.41007	0.05737	kg 1,4-DCB
Ionizing radiation	1.69044	0.06541	kBq Co-60 eq
Mineral resource scarcity	0.19245	0.00818	kg Cu eq

Some of these impacts are expressed by LCA indicators (Table 5), but other supply-side impacts related to the environmental support demand at the scale of the biosphere (resource generation, renewability time, etc.) are not, and they require a different conceptual framework, such as EMA. However, in agricultural studies, most EMA researchers still use values for agricultural chemicals deriving from obsolete evaluations, such as UEVs of generic fertilizers, pesticides and herbicides, respectively from Odum [11], Brandt-Williams [20], Dong et al. [87], simply adjusted to the most recent GEB. It is therefore crucial to address a more accurate emergy evaluation of all chemicals used in agriculture. The integration of LCA and EMA is helpful to achieve such important goal.

Quantifying changes in resource utilization and assessing the broader and multi-dimensional environmental impacts brought by these changes thanks to updated UEVs integrated to LCA indicators may help policy adjustment, re-formulation and monitoring. In fact, while LCA assessments shed light on the achieved advantages in terms of lower human health and ecosystem impacts, updated UEVs coupled to other and consequently more reliable emergy indicators add to the assessment the awareness of lower demand for environmental services and resource generation, in so providing an integrated upstream and downstream picture in support to more sustainable agricultural policy making.

UEV is a parameter to evaluate the environmental efficiency of a production process. The calculated UEV of glyphosate in this study was 3.9 times as much as the UEV of herbicides from Ghisellini et al. [13] (6.25E+12 sej/kg, djusted to the most recent GEB). UEVs of electricity and sodium hydroxide calculated in this study are also higher than the UEVs from previous studies (see Table 4). A higher UEV means lower environmental efficiency, which cannot be ignored or disregarded. During the calculation, a large number of non-renewable resources were found to be invested in the production process, such as heat and electricity from coal and natural gas and underground minerals, which entail increasing environmental costs, namely decreasing renewability. Data revealed the need for improvement in resources allocation and management in order to achieve sustainable development and, once again, a more sustainable agriculture.

4.2. Feasibility and improvement of calculation methods

In this study, with the detailed data support of the Ecoinvent database, UEVs were calculated for glyphosate and urea (adjusted to China production processes). UEVs of intermediate chemicals such as ammonia, acetic anhydride, chlorine gas, formaldehyde, phosphorous chloride, and sodium hydroxide were also calculated. These chemicals are commonly used in many other industrial processes too, not just agricultural chemistry. Ammonia is a building block for the synthesis of many pharmaceutical products and it is used in a large number of commercial cleaning products [88,89]. Acetic anhydride is also widely used as a reagent in organic synthesis [90]. Therefore, a more robust UEV calculation method based on LCA databases provides reliable UEVs for the assessment of many other processes and, as a consequence, more reliable emergy indicators to investigate the upstream sustainability of production processes, most often disregarded.

The industrial production of chemicals is not only dependent on renewable inputs, but also, to a far greater degree, on nonrenewable fossil fuels and mineral resources available underground. The novelty of all the calculations performed in this study is the use of these basic (elementary) flows in EMA and LCA databases as the starting point, in order to calculate characterization factors and indicators for intermediate and final products, consistent with the basic rules of the two methods. Luckily, as already occurred with LCA calculation of so–called "product flows" starting from "elementary flows", also in EMA most basic UEVs of "elementary" flows of renewable resources, basic minerals and fuels have already been calculated [11,58,75] and can serve as the starting point for more reliable further calculations through the integrated procedure described in the present work. Further, there is also an online database [91] that presently contains nearly 1000 entries, in addition to a large number of UEVs available in the EMA literature, waiting to be updated and perhaps revised. The advancement of these basic pieces of work will improve the applicability of the EMA calculation method. As mentioned previously in the Methods section, a crucial and much needed improvement relies on the integration of the EMA and LCA frameworks, as advocated by many emergy and LCA practitioners [40–43]. The present study provides a robust demonstration of how to deal with allocation and algebraic rules in an integrated approach, as an additional step towards a dedicated integrated software package. This is, arguably, one of the most urgent tasks for LCA and EMA practitioners, in order to support the sustainable use of resources in production and consumption sectors from both upstream and downstream points of view.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this manuscript.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.rser.2021.111604.

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Ethics approval

The Authors declare that there are no ethical conflicts associated to the submitted manuscript.

Consent to participate

All authors have been allowed by their affiliation Organizations to collaborate to this manuscript.

Consent for publication

All authors have been allowed by their affiliation Organizations to submit this manuscript.

Availability of data and material

Appropriate reference was given for all the data used in the submitted manuscript. However, Authors remain available to further clarifications if contacted by interested readers.

Code availability (software application or custom code): not applicable.

Authors' contributions

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Supplementary Material

Environmental Cost and Impacts of Chemicals Used in Agriculture: An Integration of Emergy and Life Cycle Assessment

Yanfeng Lyu[1], Marco Raugei[2] , Xiaohong Zhang[1], Salvatore Mellino[3], Sergio Ulgiati[3,4,*]

[1] College of Environmental Sciences, Sichuan Agricultural University-Chengdu Campus, Chengdu, Sichuan 611130, PR China

[2] Oxford Brookes University, UK

[3] Department of Science and Technology, Parthenope University of Naples, Centro Direzionale -Isola C4, 80143, Napoli, Italy

[4] School of Environment, Beijing Normal University, Beijing, 100085, PR China

1 Figures and figure explanation

1.1 Geobiosphere systemic diagram with main components and driving forces

Brown and Ulgiati (Figure S1) point out how the self–organization of the geobiosphere took place over million years of evolution. The main geobiosphere sectors (atmosphere, oceans and lithosphere) interact synergically supported by the main driving forces (solar radiation, deep heat and gravitational potential) and support the different forms of life phenomena in the planet, releasing low temperature heat to the outer space. The three main driving forces can be expressed in one unit only, that Odum identified as solar emergy joule (sej) and added into a total emergy annually supporting the planet and its physical and biological phenomena.

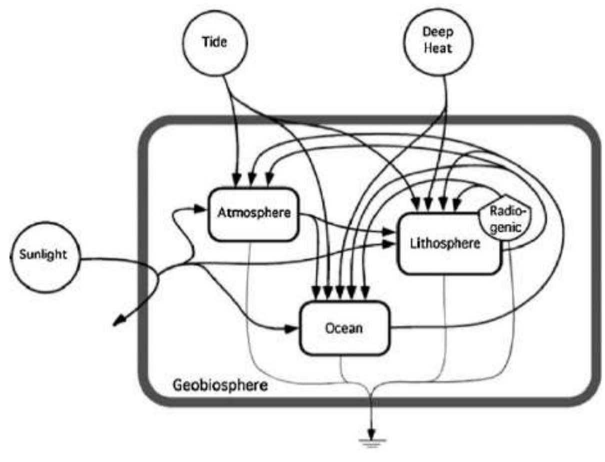

Figure S1. Earth geobiosphere, a hierarchical web of components connected by flows of available energy, materials, and information that build potential energy and circulate materials [1].

* Corresponding Author. E-mail: sergio.ulgiati@uniparthenope.it

1.2 LCA diagram showing interaction among the different steps

LCA is a complex procedure (Figure S2), where resource use and products are investigated in order to evaluate costs and benefits of the process. Core of the LCA is the inventory of input and output flows (resources, products, emissions). Crucial in the assessment is the reference of the input flows and impacts to a so–called "functional unit", namely the quantified performance of the process to which all inflows and outflows are referred. The result of an LCA is the calculation of impacts generated by the investigated product. In the presence of more than one product, all inflows and impacts are allocated to each of them in proportion to some of their physical or economic characteristics (e.g. mass or energy content or economic value) [2].

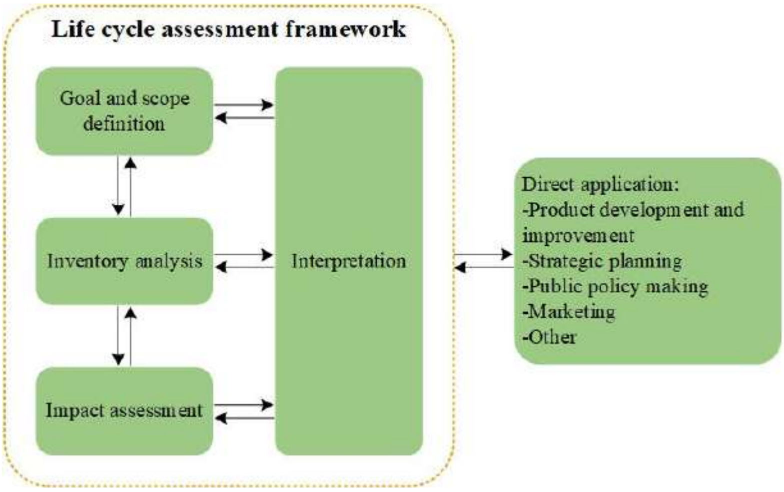

Figure S2. The four steps of LCA, mutually interacting and reinforcing, until the final result is achieved (impacts of the investigated process) and used for policy making, planning, marketing [2].

1.3 Flow chart of the investigated process

The flow chart in Figure S3 shows the main supply and production chains of urea and glyphosate from underground minerals and fossil fuels. The diagram only shows the main patterns, without focusing on emissions of waste heat and chemicals. Further, renewable flows and inflows of labor and services are also disregarded. Productive interactions among flows within each sub–production processes are not shown (see Figure 1 in text).

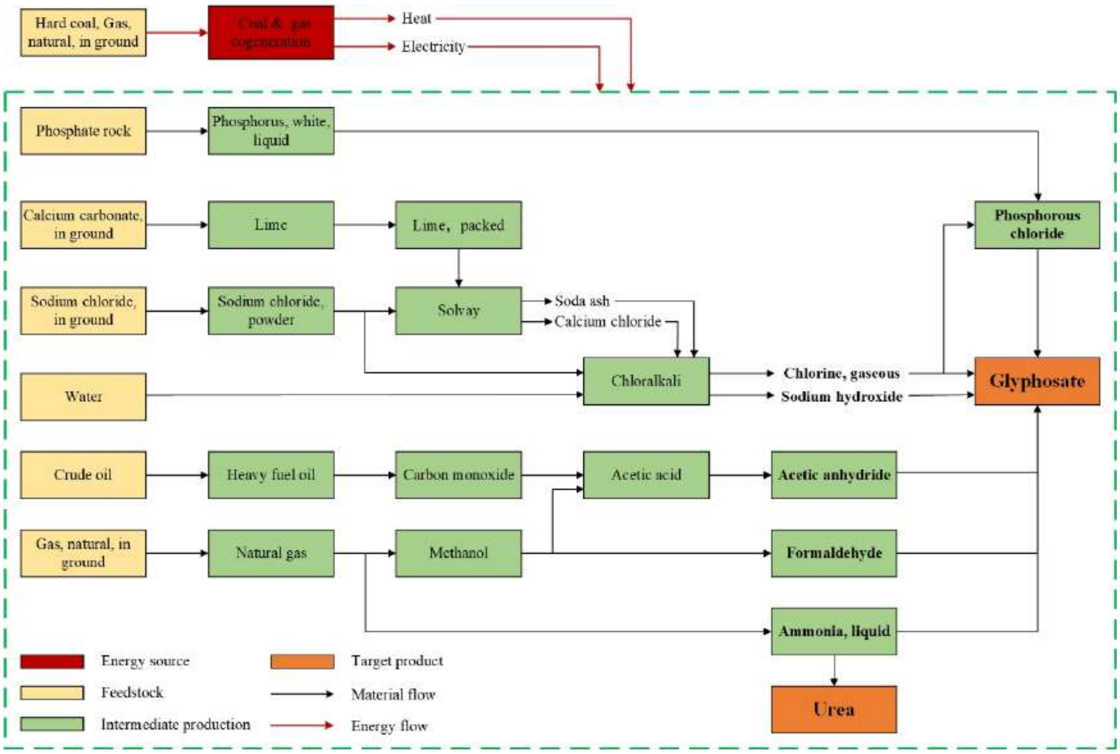

Figure S3. Conventional flow–chart diagram of urea and glyphosate production.

2 Tables and table explanation

2.1 Lists of tables

Table S15 UEV calculation of carbon monoxide

Table S16 UEV calculation of methanol

Table S17 UEV calculation of ammonia

Table S18 UEV calculation of chlorine gaseous

Table S19 UEV calculation of soda ash, light, crystalline, heptahydrate

Table S20 UEV calculation of calcium chloride

Table S21 UEV calculation of lime, packed

Table S22 UEV calculation formaldehyde

Table S23 UEV calculation of phosphorous chloride

Table S24 UEV calculation of phosphorus, white, liquid

Table S25 UEV calculation of sodium hydroxide

Table S26 UEV calculation of sodium chloride, powder

2.2 Calculation of UEVs of electricity

Tables S1-S7 show the calculation processes for a range of energy carriers and the UEVs of electricity produced by various technologies are shown in Table S8. The UEV of thermal electricity primarily depends on the feedstock used to generate electricity; therefore, in first approximation, the UEVs for coal- gas- and nuclear electricity are calculated here on the basis of the emergy in the feedstock only, plus water for cooling.

The overall average UEV of Chinese electricity was calculated based on the power station data from official website of IEA Sankey Diagram [3]. There are the following categories of power: coal, hydropower, wind, nuclear, oil, natural gas, biofuels and waste. Weighting factors for all electricity generation technologies were determined, based on the amounts of electricity produced in the year 2018, to calculate the mean UEV of electricity in China, as follows:

$$UEV_{electricity} = UEV_i \times \partial_i$$

Where UEV_i and ∂_i are UEV of "i-th" type electricity and weight of "i-th" type, respectively.

In China, the share of thermal power plants in the grid mix is proximately 80%, therefore the calculation results for the grid mix is close to the UEV of thermal electricity, at 2.85E+05 sej/J.

2.3 Calculation of UEVs of transportation modes

Due to the distance and carrying capacity, different transportation modalities need to be selected. We divide it into four categories: freight train, light commercial vehicle, freight lorry and freight transoceanic ship. UEVs of different transport modalities were shown in Table S9-S12. Using the Ecoinvent database to trace the source step by step, we found that the UEV of transportation was mainly determined by the energy carrier used, including diesel, petrol, electricity and heavy fuel oil. In other words, the accurate UEVs of energy could help us accurately calculate the UEVs of transport modalities. On the other hand, Ecoinvent database allowed detailed classification of transportation, which also helped to improve the calculation accuracy of UEV.

2.4 Calculation of UEVs of intermediate chemicals

Table S13 - S26 provided detailed calculation information of intermediate chemicals, such as acetic anhydride, acetic acid, carbon monoxide. They are all foundational UEVs for the accurate calculation of the UEVs of glyphosate and urea.

Table S1. UEV calculation of heat (natural gas)

Flow (LCA Ecoinvent v3.1)	Amount	Unit	UEV (sej/unit)	Emergy (sej)	References
Inputs					
Electricity	4.21E+03	J	2.85E+05	1.20E+09	Table S8
Natural gas	1.77E-02	kg	7.46E+12	1.32E+11	[4]
Output					
Heat, district or industrial, natural gas	1	MJ			
Total emergy of heat, district or industrial, natural gas				1.33E+11	
UEV of heat, district or industrial, natural gas			1.33E+11		

Note: Input and output data referred from Ecoinvent v3.1 (heat production, natural gas, at industrial furnace >100kW -RoW)

Table S2. UEV calculation of heat (other than natural gas)

Flow (LCA Ecoinvent v3.1)	Amount	Unit	UEV (sej/unit)	Emergy (sej)	References
Inputs					
Electricity	1.88E+04	J	2.85E+05	5.36E+09	Table S8
Hard coal	4.32E-02	kg	2.25E+12	9.73E+10	[4]
Output					
Heat, district or industrial, other than natural gas	1	MJ			

Total emergy of heat, district or industrial, other than natural gas				1.03E+11	
UEV of heat, district or industrial, other than natural gas			1.03E+11		

Note: Input and output data referred from Ecoinvent v3.1 (heat production, at hard coal industrial furnace 1-10MW -RoW)

Table S3. UEV calculation of electricity-coal [5]

Flow (LCA Ecoinvent v3.1)	Amount	Unit	UEV (sej/unit)	Emergy (sej)	References
Inputs					
Hard coal	4.58E-01	kg	2.25E+12	1.03E+12	[4]
Water	4.78E-02	m3	1.00E+11	4.80E+09	[4]
Output					
Electricity	1	kWh			
Total emergy of electricity				1.03E+12	
UEV of total emergy of electricity		kWh	1.03E+12		
UEV of total emergy of electricity		J	2.87E+05		

Note: Input and output data referred from Ecoinvent v3.1 (electricity production, hard coal -CN)

Table S4. UEV calculation of electricity-nuclear [5]

Flow (LCA Ecoinvent v3.1)	Amount	Unit	UEV (sej/unit)	Emergy (sej)	References
Inputs					
Water	7.95E-02	m3	1.00E+11	7.99E+09	[4]
Heat, U235 fission, converted to Uranium mineral	0.9	kg	1.54E+12	1.39E+12	
Output					
Electricity	1	kWh			
Total emergy of electricity				1.39E+12	
UEV of electricity		kWh	1.39E+12		
UEV of electricity		J	3.87E+05		

Notes: The fission of one gram of U235 releases 68 GJ of heat. However, in order to have one pure gram of U235 about 7 ton of Uranium mineral need to be excavated. In general, the mineral is fed to the power plant after a process of enrichment of the U235 fraction from 0.7% to about 5%. After this is done, the heat release of one kg of Uranium enriched mineral is 10 MJ/kg. The heat produced by the Uranium is converted into electricity with an average efficiency of 40%. So ,1 kWh (3.6 MJ) of electricity need heat 9 MJ, equal to Uranium mineral 900g.

Table S5. UEV calculation of electricity-natural gas [5]

Flow (LCA Ecoinvent v3.1)	Amount	Unit	UEV (sej/unit)	Emergy (sej)	References
Inputs					
Natural gas	1.95E-01	kg	7.80E+12	1.52E+12	[4]
Water	6.85E-02	m3	1.00E+11	6.89E+09	
Water, decarbonized, at user	2.32E+00	kg	1.03E+08	2.40E+08	
Output					

Electricity	1	kWh			
Total emergy of electricity				1.53E+12	
UEV of electricity		kWh	1.53E+12		
UEV of electricity		J	4.25E+05		

Note: Input and output data referred from Ecoinvent v3.1 (electricity production, natural gas, at conventional power plant - CN)

Table S6. UEV calculation of heavy fuel oil [5]

Flow (LCA Ecoinvent v3.1)	Amount	Unit	UEV (sej/unit)	Emergy (sej)	References
Inputs					
Electricity	1.24E+05	J	2.81E+05	3.50E+10	Table S8
Heat, district or industrial, other than natural gas	1.66E+00	MJ	1.03E+11	1.71E+11[a]	Table S2
Heavy fuel oil, burned in refinery furnace	5.71E-01	MJ	1.63E+11	9.33E+10	Table S7
Naphtha	4.22E-02	kg	6.68E+12	2.82E+11	
Petroleum	1.06E+00	kg	5.79E+12	6.14E+12	[4]
Water	5.00E-03	m3	1.00E+11	5.02E+08	
Output					
Heavy fuel oil	1	kg			
Total emergy of heavy fuel				6.72E+12	
UEV of heavy fuel oil		kg	6.72E+12		

Note: Input and output data referred from Ecoinvent v3.1 (petroleum refinery operation - RoW)

[a] assume the heat is from coal

Table S7. UEV calculation of heavy fuel oil, burned in refinery furnace [5]

Flow (LCA Ecoinvent v3.1)	Amount	Unit	UEV (sej/unit)	Emergy (sej)	References
Input					
Heavy fuel oil	2.43E-02	kg	6.72E+12	1.63E+11	Table S6
Output					
Heavy fuel oil, burned in refinery furnace	1	MJ			
UEV of heavy fuel oil, burned in refinery furnace		MJ	1.63E+11	1.63E+11	

Note: Input and output data referred from Ecoinvent v3.1 (Heavy fuel oil, burned in refinery furnace - RoW)

Table S8. UEV calculation of electricity [5]

Items	UEV (sej/unit)	Unit	Weight (Chinese grid mix)	References
Electricity-coal	2.87E+05	J	79.49%	Table S3
Electricity-hydropower	2.47E+05	J	7.28%	[6]
Electricity-wind	3.41E+04	J	2.72%	[7]
Electricity-nuclear	3.87E+05	J	4.78%	Table S4
Electricity-oil	4.03E+05	J	0.44%	[8]
Electricity-natural gas	4.25E+05	J	2.87%	Table S5
Electricity-biofuels and waste	-	-	2.43%	-
Electricity-mean	2.85E+05	J		

Table S9. UEV calculation of light vehicle [5]

Flow (LCA Ecoinvent v3.1)	Amount	Unit	UEV (sej/unit)	Emergy	References
Inputs					
Diesel, low-sulfur	3.18E-01	kg	7.26E+12	2.31E+12	[4]
Petrol, low-sulfur	7.53E-02	kg	7.02E+12	5.28E+11	[4]
Output					
Transport, freight light vehicle	1	t*km			
Total emergy of transport, freight light vehicle					2.84E+12
UEV of Transport, freight light vehicle			2.84E+12		

Note: Input and output data referred from Ecoinvent v3.1 (transport, freight, light commercial vehicle - RoW)

Table S10. UEV calculation of freight train [5]

Flow (LCA Ecoinvent v3.1)	Amount	Unit	UEV (sej/unit)	Emergy	References
Inputs					
Diesel	6.77E-04	kg	7.26E+12	4.92E+09	[4]
Electricity	1.29E+05	J	2.85E+05	3.63E+10	Table S8
Output					
Transport, freight train	1	t*km			
Total emergy of transport, freight train				4.12E+10	
UEV of transport, freight train			4.12E+10		

Note: Input and output data referred from Ecoinvent v3.1 (transport, freight train, electricity - RoW)

Table S11. UEV calculation of freight lorry [5]

Flow (LCA Ecoinvent v3.1)	Amount	Unit	UEV (sej/unit)	Emergy	References
Inputs					
Transport, freight, lorry 16-32 metric ton	3.40E-01	t*km	2.75E+11	9.34E+10	
Transport, freight, lorry 3.5-7.5 metric ton	4.00E-02	t*km	8.07E+11	3.23E+10	
Transport, freight, lorry 7.5-16 metric ton	0.03	t*km	3.49E+11	1.05E+10	
Transport, freight, lorry >32 metric ton	0.59	t*km	1.25E+11	7.40E+10	
Output					
Transport, freight lorry	1	t*km			
Total emergy of transport, freight lorry				2.10E+11	
UEV of transport, freight lorry			2.10E+11		

Note: Input and output data referred from Ecoinvent v3.1 (transport, freight train, electricity - RoW)

Table S12. UEV calculation of freight ship [5]

Flow (LCA Ecoinvent v3.1)	Amount	Unit	UEV (sej/unit)	Emergy	References
Inputs					
Heavy fuel oil	2.50E-03	kg	6.72E+12	1.68E+10	Table S6
Output					
Transport, freight ship	1	t*km			
Total emergy of transport, freight ship				1.68E+10	
UEV of transport, freight ship			1.68E+10		

Note: Input and output data referred from Ecoinvent v3.1 (transport, freight, sea, transoceanic ship - GLO)

Table S13. UEV calculation of acetic anhydride

Flow (LCA Ecoinvent v3.1)	Amount	Unit	UEV (sej/unit)	Emergy (sej)	References
Inputs					
Acetic acid, without water, in 98% solution state	1.27E+00	kg	8.02E+12	1.02E+13	Table S14
Electricity, medium voltage	1.31E+06	J	2.85E+05	3.75E+11	Table S8
Water	3.73E-01	m3	1.00E+11	3.75E+10	[4]
Heat, district or industrial, nature gas	7.72E+00	MJ	1.33E+11	1.03E+12	Table S1
Heat, district or industrial, other than nature gas	4.43E+00	MJ	1.03E+11	4.54E+11	Table S2
Transport, freight train	3.09E-01	t*km	4.17E+10	1.29E+10	Table S10
Transport, freight, lorry	2.09E-01	t*km	2.10E+11	4.39E+10	Table S11
Transport, freight, s ship & inland waterways	6.24E-01	t*km	1.68E+10	1.05E+10	Table S12
Output					
Acetic anhydride	1.00E+00	kg			
Total emergy of acetic anhydride				1.18E+13	
UEV of acetic anhydride			1.18E+13		

Note: Input and output data referred from Ecoinvent v3.1 (acetic anhydride production, ketene route – RoW)

Table S14. UEV calculation of acetic acid

Flow (LCA Ecoinvent v3.1)	Amount	Unit	UEV (sej/unit)	Emergy (sej)	References
Inputs					
Carbon monoxide	4.81E-01	kg	6.80E+12	3.27E+12	Table S15
Electricity	2.47E+05	J	2.85E+05	7.05E+10	Table S8
Heat, district or industrial, nature gas	1.10E+00	MJ	1.33E+11	1.47E+11	Table S1
Heat, district or industrial, other than nature gas	6.15E-01	MJ	1.03E+11	6.31E+10	Table S2
Methanol	5.05E-01	kg	8.82E+12	4.45E+12	Table S16
Water	7.82E-02	m^3	1.00E+11	7.85E+09	[4]
Transport, freight train	3.09E-01	t*km	4.17E+10	1.29E+10	Table S10
Transport, freight lorry	2.09E-01	t*km	2.10E+11	4.39E+10	Table S11
Transport, freight ship & inland waterways	6.24E-01	t*km	1.68E+10	1.05E+10	Table S12
Output					
Acetic acid, without water, in 98% solution state	1	kg			
Total emergy of acetic acid				8.02E+12	
UEV of acetic acid			8.02E+12		

Note: Input and output data referred from Ecoinvent v3.1 (acetic acid production, product in 98% solution state – RoW)

Table S15. UEV calculation of carbon monoxide

Flow (LCA Ecoinvent v3.1)	Amount	Unit	UEV (sej/unit)	Emergy (sej)	References
Inputs					
Electricity	8.28E+06	J	2.85E+05	2.36E+12	Table S8
Heavy fuel oil	6.60E-01	kg	6.72E+12	4.44E+12	Table S6
Output					
Carbon monoxide	1	kg			
Total emergy of carbon monoxide				6.80E+12	
UEV of carbon monoxide			6.80E+12		

Note: Input and output data referred from Ecoinvent v3.1 (carbon monoxide production – RoW)

This report assumes that CO is produced from partial combustion of heavy heating oil. The inventory is based on assumed production figures from a planned plant.

Table S16. UEV calculation of methanol

Flow (LCA Ecoinvent v3.1)	Amount	Unit	UEV (sej/unit)	Emergy (sej)	References
Inputs					
Electricity	2.66E+05	J	2.85E+05	7.60E+10	Table S8
Heat, district or industrial, natural gas	6.93E+00	MJ	1.33E+11	9.24E+11	Table S1
Molybdenum	1.03E-01	kg	3.20E+09	3.29E+08	[4]
Natural gas	9.94E-01	kg	7.80E+12	7.75E+12	
Water, cooling, unspecified natural origin	9.86E-03	m^3	1.00E+11	9.91E+08	
Zinc	3.00E-05	kg	1.07E+13	3.20E+08	
Transport, freight train	3.09E-01	t*km	4.17E+10	1.29E+10	Table S10
Transport, freight lorry	2.09E-01	t*km	2.10E+11	4.39E+10	Table S11
Transport, freight ship & inland waterways	6.24E-01	t*km	1.68E+10	1.05E+10	Table S12
Output					
Methanol	1	kg			
Total emergy of methanol				8.82E+12	
UEV of methanol			8.82E+12		

Note: Input and output data referred from Ecoinvent v3.1 (methanol production - GLO)

The process describes the production of methanol from natural gas.

Table S17. UEV calculation of ammonia [5]

Flow (LCA Ecoinvent v3.1)	Amount	Unit	UEV (sej/unit)	Emergy (sej)	References
Inputs					
Heavy fuel oil	1.97E-01	kg	6.72E+12	1.32E+12	Table S6
Natural gas	3.94E-01	kg	7.80E+12	3.07E+12	[4]
Water	1.41E-01	m^3	1.00E+11	1.42E+10	[4]
Electricity	2.50E+05	J	2.85E+05	7.12E+10	Table S8
Transport, freight train	2.76E-01	t*km	4.17E+10	1.15E+10	Table S10
Transport, freight lorry	1.49E-01	t*km	2.10E+11	3.12E+10	Table S11
Transport, freight ship & inland waterways	8.88E-01	t*km	1.68E+10	1.49E+10	Table S12
Output					

Ammonia, liquid	1	kg			
Total emergy of ammonia				4.54E+12	
UEV of Ammonia, liquid			4.54E+12		

Note: Input and output data referred from Ecoinvent v3.1 (ammonia production, steam reforming, liquid – RoW)

The process describes the production of ammonia from steam reforming.

Table S18. UEV calculation of chlorine gaseous

Flow (LCA Ecoinvent v3.1)	Amount	Unit	UEV (sej/unit)	Emergy (sej)	References
Inputs					
Barite	1.38E-03	kg	5.09E+11	1.52E+09	[4]
Calcium chloride	7.01E-03	kg	1.27E+12	1.93E+10	Table S20
Electricity	5.08E+06	J	2.85E+05	3.15E+12	Table S8
Soda ash, light, crystalline, heptahydrate	4.53E-03	kg	1.20E+12	1.18E+10	Table S19
Sodium chloride, powder	6.89E-01	kg	2.44E+11	3.66E+11	Table S26
Sodium hydroxide, without water, in 50% solution state	7.88E-04	kg	2.97E+12	5.09E+09	Table S25
Water	1.15E-01	m3	1.00E+11	2.51E+10	[4]
Transport, freight lorry	2.09E-02	t*km	2.10E+11	9.54E+09	Table S11
Transport, freight train	3.09E-02	t*km	4.17E+10	2.80E+09	Table S10
Output					
Chlorine, gaseous	1	kg			
Total emergy of chlorine gaseous				3.58E+12	
UEV of chlorine gaseous			3.58E+12		

Note: Input and output data referred from Ecoinvent v3.1 (chlor-alkali electrolysis, diaphragm cell – RoW)

In industry, elemental chlorine is usually produced by the electrolysis of sodium chloride dissolved in water. Along with chlorine, the method yields hydrogen gas and sodium hydroxide. An allocation to the two products is done by mass, resulting in chlorine 46% and sodium hydroxide 52%. In the calculation, emergy of each input has been allocated with the share of 46%.

Table S19. UEV calculation of soda ash, light, crystalline, heptahydrate

Flow (LCA Ecoinvent v3.1)	Amount	Unit	UEV (sej/unit)	Emergy (sej)	References
Inputs					
Ammonia, liquid	5.72E-04	kg	4.54E+12	7.87E+09	Table S17
Electricity	1.14E+04	J	2.85E+05	3.26E+09[a]	Table S8
Heat, district or industrial, other than natural gas	2.07E+00	MJ	1.03E+11	6.42E+11[b]	Table S2
Lime, packed	3.43E-01	kg	1.78E+10	1.85E+10	Table S21
Sodium chloride, powder	4.29E-01	kg	2.44E+11	3.18E+11	Table S26
Water	3.04E-02	m^3	1.00E+11	9.24E+09	[4]
Transport, freight train	3.09E-01	t*km	4.17E+10	3.91E+10	Table S10
Transport, freight lorry	2.09E-01	t*km	2.10E+11	1.33E+11	Table S11

Transport, freight ship & inland waterways	6.24E-01	t*km	1.68E+10	3.17E+10	Table S12
Output					
Soda ash, light, crystalline, heptahydrate	1	kg			
Total emergy of soda ash, light, crystalline, heptahydrate				1.20E+12	
UEV of soda ash, light, crystalline, heptahydrate			1.20E+12		

Note: Input and output data referred from Ecoinvent v3.1 (soda production, solvay process – RoW)

The multioutput process "soda production, Solvay process, at plant" delivers the co-products "soda, powder, at plant" and "calcium chloride, $CaCl_2$, at plant". An allocation to the two products is done by using the prices, resulting in soda 33% and calcium chloride 67%. In the calculation, emergy of each input has been allocated with the share of 33%.

[a] and [b] are co-products

Table S20. UEV calculation of calcium chloride

Flow (LCA Ecoinvent v3.1)	Amount	Unit	UEV (sej/unit)	Emergy (sej)	References
Inputs					
Ammonia, liquid	1.36E-03	kg	4.54E+12	9.21E+09	Table S17
Electricity	9.79E+04	J	2.85E+05	4.17E+10[a]	Table S8
Heat, district or industrial, other than natural gas	4.91E+00	MJ	1.03E+11	7.52E+11[b]	Table S2
Lime, packed	8.16E-01	kg	1.78E+10	2.16E+10	Table S21
Sodium chloride, powder	1.02E+00	kg	2.44E+11	3.72E+11	Table S26
Water	7.22E-02	m^3	1.00E+11	1.08E+10	[4]
Transport, freight train	3.09E-01	t*km	4.17E+10	1.92E+10	Table S10
Transport, freight lorry	2.09E-01	t*km	2.10E+11	6.55E+10	Table S11
Transport, freight ship & inland waterways	6.24E-01	t*km	1.68E+10	1.56E+10	Table S12
Output					
Calcium chloride	1	kg			
Total emergy of calcium chloride				1.27E+12	
UEV of calcium chloride			1.27E+12		

Note: Input and output data referred from Ecoinvent v3.1 (soda production, solvay process – RoW)

The multioutput process "soda production, Solvay process, at plant" delivers the co-products "soda, powder, at plant" and "calcium chloride, $CaCl_2$, at plant". An allocation to the two products is done by using the prices, resulting in soda 33% and calcium chloride 67%. In the calculation, emergy of each input has been allocated with the share of 67%.

[a] and [b] are co-products.

Table S21. UEV calculation of lime, packed

Flow (LCA Ecoinvent v3.1)	Amount	Unit	UEV (sej/unit)	Emergy (sej)	References
Inputs					

Lime	1.01E+00	kg	1.72E+10	1.73E+10	[4]
Heat, central or small-scale, other than natural gas	1.41E-03	MJ	1.03E+11	1.45E+08	Table S2
Water	2.80E-03	m^3	1.00E+11	2.81E+08	[4]
Output					
Lime, packed	1	kg			
Total emergy of lime, packed				1.78E+10	
UEV of lime, packed			1.78E+10		

Note: Input and output data referred from Ecoinvent v3.1 (lime production, milled, packed – RoW)

Table S22. UEV calculation formaldehyde

Flow (LCA Ecoinvent v3.1)	Amount	Unit	UEV (sej/unit)	Emergy (sej)	References
Inputs					
Electricity	4.68E+05	J	2.85E+05	1.33E+11	Table S8
Methanol	1.04E+00	kg	8.82E+12	9.17E+12	Table S16
Transport, freight train	3.09E-01	t*km	4.17E+10	1.29E+10	Table S10
Transport, freight lorry	2.09E-01	t*km	2.10E+11	4.39E+10	Table S11
Transport, freight ship & inland waterways	6.24E-01	t*km	1.68E+10	1.05E+10	Table S12
Output					
Formaldehyde	1	kg			
Total emergy of formaldehyde				9.37E+12	
UEV of formaldehyde			9.37E+12		

Note: Input and output data referred from Ecoinvent v3.1 (oxidation of methanol – RoW)

Table S23. UEV calculation of phosphorous chloride

Flow (LCA Ecoinvent v3.1)	Amount	Unit	UEV (sej/unit)	Emergy (sej)	References
Inputs					
Chlorine, gaseous	7.90E-01	kg	3.58E+12	2.83E+12	Table S18
Electricity	1.20E+06	J	2.85E+05	3.98E+11	Table S8
phosphorus, white, liquid	2.26E-01	kg	1.76E+13	3.34E+12	Table S24
Transport, freight train	3.09E-01	t*km	4.17E+10	1.29E+10	Table S10
Transport, freight lorry	2.09E-01	t*km	2.10E+11	4.39E+10	Table S11
Transport, freight ship & inland waterways	6.24E-01	t*km	1.68E+10	1.05E+10	Table S12
Output					
Phosphorous chloride	1	kg			
Total emergy of phosphorous chloride				7.21E+12	
UEV of phosphorous chloride			7.21E+12		

Note: Input and output data referred from Ecoinvent v3.1 (phosphorous chloride production – RoW)

Table S24. UEV calculation of phosphorus, white, liquid

Flow (LCA Ecoinvent v3.1)	Amount	Unit	UEV (sej/unit)	Emergy (sej)	References

Inputs					
Electricity	4.68E+07	J	2.85E+05	1.33E+13[a]	Table S8
Gravel, crushed	2.80E+00	kg	4.62E+10	1.29E+11	[4]
Hard coal	1.25E+00	kg	2.25E+12	2.81E+12[b]	
Phosphate rock, as P_2O_5	8.00E+00	kg	1.56E+11	1.25E+12	
Water	3.40E-02	m^3	1.00E+11	3.42E+09	
Transport, freight train	3.09E-01	t*km	4.17E+10	1.29E+10	Table S10
Transport, freight lorry	2.09E-01	t*km	2.10E+11	4.39E+10	Table S11
Transport, freight ship & inland waterways	6.24E-01	t*km	1.68E+10	1.05E+10	Table S12
Flow					
Output					
Phosphorus, white, liquid	1	kg			
Total emergy of phosphorus, white, liquid				1.76E+13	
UEV of phosphorus, white, liquid			1.76E+13		

Note: Input and output data referred from Ecoinvent v3.1 (phosphorus production, white, liquid – RoW)

Large uncertainty of the process data due to weak data on the production process (based only on literature values)

Table S25. UEV calculation of sodium hydroxide

Flow (LCA Ecoinvent v3.1)	Amount	Unit	UEV (sej/unit)	Emergy (sej)	References
Inputs					
Barite	1.42E-03	kg	5.09E+11	1.39E+09	[4]
Calcium chloride	7.24E-03	kg	1.27E+12	1.76E+10[a]	Table S20
Electricity	4.35E+06	J	2.85E+05	2.38E+12	Table S8
Soda ash, light, crystalline, heptahydrate	7.12E-01	kg	2.44E+11	3.34E+11[b]	Table S19
Sodium chloride, powder	4.68E-03	kg	1.20E+12	1.08E+10	Table S26
Sodium hydroxide, without water, in 50% solution state	1.71E-02	kg	2.97E+12	9.77E+10	Table S25
Water	4.14E-02	m3	1.00E+11	8.01E+09	[4]
Transport, freight lorry	6.24E-01	t*km	1.68E+10	2.01E+10	Table S11
Transport, freight train	3.09E-01	t*km	4.17E+10	2.48E+10	Table S12
Output					
Sodium hydroxide, without water, in 50% solution state	1	kg			
Total emergy of sodium hydroxide				2.97E+12	
UEV of sodium hydroxide			2.97E+12		

Note: Input and output data referred from Ecoinvent v3.1 (chlor-alkali electrolysis, diaphragm cell-sodium hydroxide – RoW)

In industry, elemental chlorine is usually produced by the electrolysis of sodium chloride dissolved in water. Along with chlorine, the method yields hydrogen gas and sodium hydroxide. An allocation to the two products is done by mass, resulting in chlorine 46% and sodium hydroxide 52%. In the calculation, emergy of each input has been allocated with the share of 52%.

[a] and [b] are co-products

Table S26. UEV calculation of sodium chloride, powder

Flow (LCA Ecoinvent v3.1)	Amount	Unit	UEV (sej/unit)	Emergy (sej)	References
Inputs					
Diesel, burned in building machine	4.28E-03	MJ	1.70E+11	7.26E+08	[4]
Electricity	6.12E+05	J	2.85E+05	1.75E+11[a]	Table S8
Heat, district or industrial, other than natural gas	1.97E-01	MJ	1.03E+11	2.02E+10[b]	Table S2
Quicklime, milled, loose	1.39E-02	kg	8.60E+08	8.60E+08	
Sodium chloride, in ground	1.00E+00	kg	1.00E+11	6.54E+08	[4]
Water	6.51E-03	m3	4.17E+10	6.51E+09	
Transport, freight train	1.56E-01	t*km	2.10E+11	3.62E+10	Table S10
Transport, freight lorry	1.72E-01	t*km	2.84E+12	1.50E+10	Table S11
Transport, freight vehicle	5.30E-03	t*km	1.68E+10	9.90E+09	Table S9
Transport, freight sea ship & inland waterways	5.89E-01	t*km	1.70E+11	7.26E+08	Table S12
Output					
Sodium chloride, powder	1	kg			
Total emergy of sodium chloride, powder				2.62E+11	
UEV of sodium chloride, powder			2.62E+11		

Note: Input and output data referred from Ecoinvent v3.1 (sodium chloride production, powder – RoW)

[a] and [b] are co-products.

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