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Assessing mass intensity as a green chemistry metric: why expanding system boundaries is not enough†

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Evaluating the environmental impacts of chemicals is crucial for a sustainable chemical industry. While Life Cycle Assessment (LCA) is recommended for evaluating environmental impacts, collecting chemical life-cycle data is often challenging. Hence, environmental performance is often approximated using simple "green chemistry metrics", particularly mass intensities like the "Process Mass Intensity" (PMI). However, despite their widespread use, mass intensities lack standardized system boundaries. Thus, this study systematically analyzes whether and with which system boundaries mass intensities can reliably approximate LCA environmental impacts. For this purpose, we evaluate Spearman correlation coefficients between sixteen LCA environmental impacts and eight mass intensities with varying system boundaries. The eight mass intensities include the (gate-to-gate) PMI and seven cradle-to-gate mass intensities considering parts of the upstream value chain, termed "Value-Chain Mass Intensity" (VCMI). For VCMI, we divide all value chain products into seven product classes and examine how including these classes in the system boundary affects the correlation. We find that expanding the system boundary from gate-to-gate to cradle-to-gate strengthens correlations for fifteen of sixteen environmental impacts. Additionally, the influence of product classes on the strength of the correlation varies depending on the environmental impact. These variations stem from a few key input materials that are represented differently across product classes, and each environmental impact is approximated by a distinct set of such materials. Consequently, a single mass-based metric cannot fully capture the multi-criteria nature of environmental sustainability. Furthermore, key input materials serve as proxies for environmental impacts because their consumption implies processes in the value chain. For instance, the input material coal implies a coal combustion process which emits carbon dioxide, making coal a key input material for approximating climate change impact. However, as processes change over time, the reliability of mass-based environmental assessment is highly time-sensitive, especially in light of the transition towards a defossilized chemical industry. We therefore question whether mass intensities should be used as a reliable proxy and suggest focusing further research on simplified LCA methods.

Green foundation

1. This work investigates under which circumstances the common practice of using mass intensities as proxies for environmental impacts is suitable, and where it fails. We show that mass intensities can be potentially unreliable for environmental assessment, particularly in light of the chemical industry's transition towards a low-carbon economy. As a consequence, we suggest that future research should focus on simplified Life Cycle Assessment (LCA) methods that more directly reflect environmental performance.
2. If the current practice of evaluating "greenness" using mass intensity metrics is misleading, then green advances reported on this basis cannot be considered reliable. Our work therefore advances green chemistry by outlining a path toward more accurate environmental assessment, helping to ensure that future green innovations genuinely reflect environmental benefits.
3. Future research could focus on simplified LCA tools tailored to specific applications where environmental assessments are essential, but LCA data or expertise are currently lacking.

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1 Introduction

Today's chemists face the challenge of developing alternative chemical processes to create a safer and environmentally benign chemical industry.[1] Yet, the environmental benefits of alternative processes are not guaranteed and must be evaluated. The recommended method to evaluate the environmental impacts of chemical processes is Life Cycle Assessment (LCA).[2,3] LCA is a holistic method that evaluates multiple environmental impacts of the entire life-cycle of chemical processes.[4,5]

While the American Chemistry Society Pharmaceutical Roundtable considers the integration of LCA methods into "green chemistry & engineering" to be a top priority, the practical application of LCA methods face several barriers,[6,7] such as:

- Extensive life-cycle data is needed, which is typically missing due to, for instance, lack of measurements or confidentiality.[8,9]
- Conducting an LCA study requires collecting and generating life-cycle data which is time-consuming and expensive.[10]

Hence, the chemical industry requires an approach to assess the environmental performance of chemical processes under limited data availability.[11]

As a practical solution in chemical development, Anastas and Warner proposed the "twelve principles of green chemistry" that can support chemists in developing "greener" chemical processes.[11,12] Some of the qualitative "green chemistry principles" are often related to quantitative "Green Chemistry Metrics" (GCMs).[13] These metrics are essentially used as indicator for the environmental performance of chemical processes and offer the advantage of needing less data compared to an LCA.[13]

Over the past decade, several authors have proposed a variety of GCMs aiming to assess the environmental performance of chemical processes.[14–17] Among all proposed GCMs, the industrial and the scientific community have selected mass intensities, *e.g.*, the Process Mass Intensity (PMI), as useful metrics to assess the environmental performance of chemical processes.[18,19] The mass intensity is a simple metric that represents the mass expenditures required to produce one kilogram of a chemical product.[20]

In contrast to the environmental impacts in LCA, *e.g. 'climate change impact'*, mass intensities do not reflect any interaction with the environment.[21,22] Instead, a mass intensity aims to provide an approximation of the environmental impacts of chemical processes based on an easy-to-determine process mass balance.[19] Evaluating the environmental performance using mass intensities assumes that lower mass expenditures result in lower environmental impacts due to: (a) less waste production, (b) higher resource efficiency,[18] and consequently, (c) less direct emissions and (d) less value chain emissions due to lower feedstock consumption. However, the assumption that mass intensities can be used as an approximation for environmental impacts cannot be generalized to all chemical processes. For instance, in the case of waste treatment, the environmental impacts of waste treatment not only depend on the amount of waste but also on the waste properties, which are typically not considered.[21] Additionally, mass intensities do not consider the origin of input materials, such as renewable materials, and completely neglect the use of energy, including renewable energy.

A recent study by Lucas *et al.* investigated the correlation between the PMI (and other GCMs) and LCA environmental impacts.[23] The authors calculated the PMI using a factory entrance to factory exit (gate-to-gate) system boundary, which is commonly applied in the literature. They found that the (gate-to-gate) PMI cannot robustly approximate LCA environmental impacts.[23] This finding confirms previous suggestions that a gate-to-gate system boundary is too limited for evaluating environmental performance through the PMI.[18,24]

The study by Lucas *et al.* further demonstrates that the supply chain involved in producing the chemicals needed for the production of the considered product can contribute significantly to the environmental impact of that product.[23] This contribution can be even more pronounced for chemicals with a longer supply chain, such as specialty chemicals and pharmaceuticals.[23] Therefore, recognizing the importance of supply chain impacts, the scientific community has advocated for a broader system boundary for PMI calculations.[18,24,25]

Jimenez-Gonzalez *et al.*[18] investigated the ability of the PMI with an extended system boundary to approximate environmental impacts by analyzing the correlation between the PMI and both greenhouse gas emissions and water usage for chemicals developed by GSK. For PMI calculation, they suggested that the PMI requires a holistic system boundary, meaning that mass expenditures of the used raw materials and intermediates should also be considered. Therefore, they expanded the system boundary beyond the factory gate and used "commonly available materials" as a starting point for PMI calculation.[18] These authors found a positive correlation between the PMI with the expanded system boundary and both greenhouse gas (GHG) emissions and water usage, *i.e.*, processes with a higher PMI tend to result in higher GHG emissions and water usage.[18] However, the authors did not provide a definition of "commonly available materials"; thus, a clear system boundary definition was still missing. Later, Roschangar *et al.* defined "commonly available materials" as GCMs system boundary based on two criteria: "*(i) the raw material is commercially available on the website of Sigma-Aldrich, and (ii) the cost of the raw material does not exceed 100 $* per *mol at the largest offered quantity*".[24]

While previous studies have explored the correlation between the PMI and environmental impacts, the current literature lacks a systematic evaluation of how different system boundaries influence this correlation. Against this background, our study systematically analyzes the impact of system boundaries on the correlation between the mass intensities and LCA environmental impacts. This study thus contributes to the field of "green chemistry" by improving the understanding under which circumstances the common practice of using mass intensities as proxies for environmental impacts is suitable, and where it fails.

For this purpose, we conducted two main analyses: (i) examining how varying system boundaries influence the correlation between mass intensities and environmental impacts, and (ii) analyzing the causal relationships to better understand what drives the correlation.

To examine the influence of system boundaries, we calculated eight distinct mass intensities with varying system boundaries (see section 2) and LCA environmental impacts for 106 chemical productions, utilizing the ecoinvent LCA database.[26] The eight mass intensities include the Process Mass Intensity (PMI), which is determined using a factory entrance to factory exit (gate-to-gate) system boundary (see section 2.2), and seven mass intensities considering parts of the upstream value chain (cradle-to-gate) (see section 2.3). A cradle-to-gate system boundary includes value chain processes, starting from the gate of the chemical production under study and extending back to the extraction of natural resources, such as crude oil or metal ores, from the environment (cradle) (see Fig. 1). We refer to these mass intensities calculated with a cradle-to-gate system boundary as Value Chain Mass Intensity (VCMI). Notably, while the materials considered in the PMI are typically intermediate products, such as chemical intermediate products, the materials of the VCMI consist exclusively of the natural resources required for the production of these intermediate products due to VCMI's cradle-to-gate system boundary (see Fig. 1). For VCMI calculations, we categorize all value chain products into seven product classes based on the Central Product Classification (CPC).[27] This product categorization enables a systematic expansion of the cradle-to-gate system boundary by stepwise including these product classes into the chemical value chain for VCMI calculation. More specifically, including a product class increases the VCMI by accounting for the additional natural resources that are required to produce the products from that product class. Based on these eight system boundaries – one gate-to-gate (PMI) and seven cradle-to-gate (VCMI) boundaries, each for a product class – we analyze the influence of system boundaries on the strength of the correlation.

Additionally, to better understand the causality underlying the correlations between environmental impacts and the VCMI, we disaggregated the VCMI into its individual components, *i.e.*, natural resources, and analyzed each resource separately. In particular, we examined the correlation between each resource and environmental impacts to identify those resources that influence the overall correlation the most. The analysis of individual resources allows inferring causal relationships between resource consumption (as considered in the VCMI) and environmental impacts. These causal relationships not only explain why there is a correlation between mass intensities and environmental impacts, but more importantly,

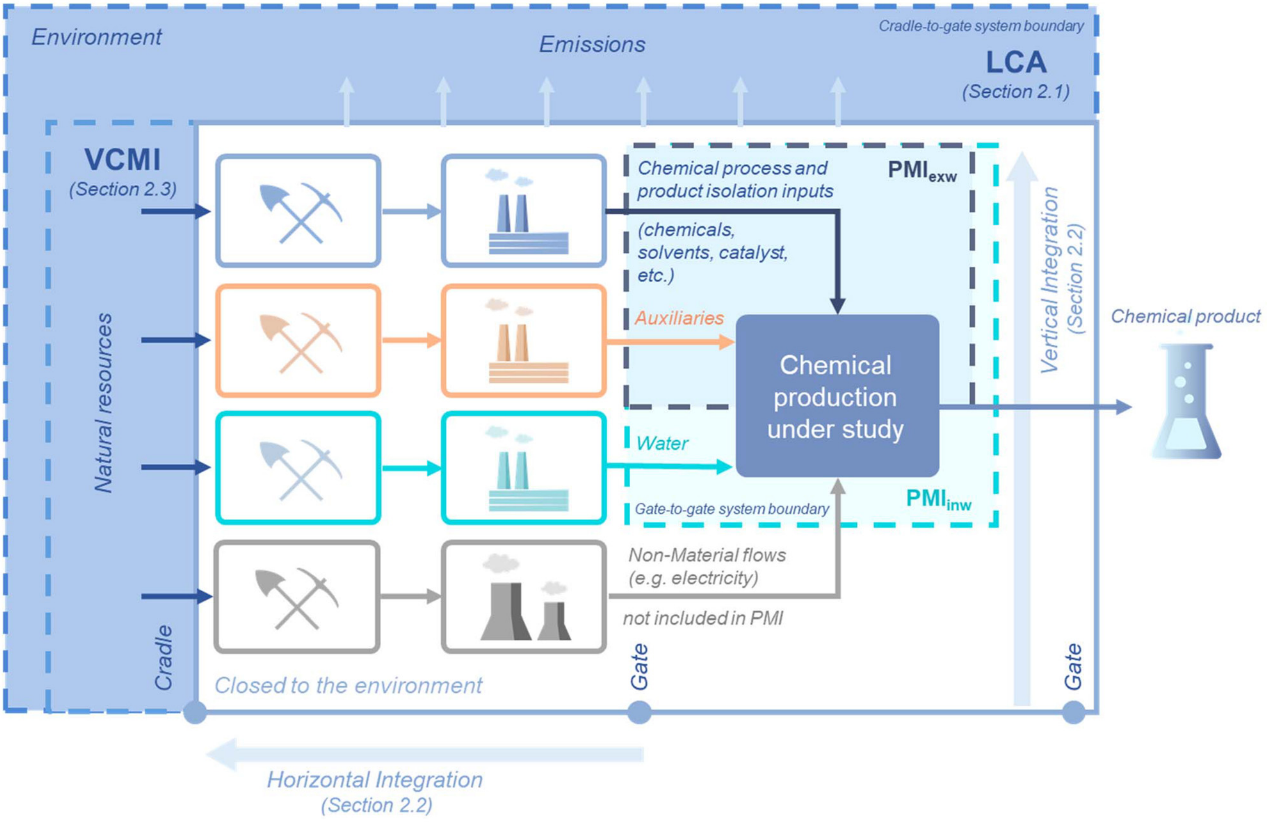

Fig. 1 System boundaries for a cradle-to-gate Life Cycle Assessment (LCA), Process Mass Intensity (PMI) (see section 2.2), and Value Chain Mass Intensity (VCMI) (see section 2.3).

they highlight the limitations mass intensities face when used for environmental assessment.

The article is structured as follows: in section 2, the methodology is presented in detail, including an introduction to LCA, mass intensities and the definition of the different system boundaries and product classes, and the correlation analysis. Section 3 contains the results and a discussion. In section 4, we finally draw our conclusions on how system boundaries influence the ability of mass intensities to capture environmental impacts, as well as the limitations mass intensities face in "green chemistry evaluation".

2 Methodology

2.1 Life cycle assessment (LCA)

LCA is a standardized method to evaluate the environmental impacts of products and services.[4] The holistic approach of LCA covers the entire life cycle of products, including raw material extraction, upstream value chain, manufacturing, packaging, use phase, and end-of-life treatment.[22]

Moreover, LCA considers multiple environmental impacts, such as '*climate change* impact', '*ecosystem toxicity*', '*fossil resource depletion*', *etc*.[22] The holistic approach of LCA helps to identify trade-offs between both life-cycle stages and environmental impacts, which makes LCA a suitable tool in various fields, such as product development, decision-making, and marketing.[22]

The system boundaries in LCA studies are defined by the ISO 14040/14044 standards.[4,5] Ideally, the system boundary of LCA covers the entire life cycle, *i.e.*, from the cradle to the grave.[4,5] However, for some LCA studies, the goal of the study can be achieved with a narrower system boundary by excluding selected sub-systems, which eases data collection compared to a full cradle-to-grave system boundary. For instance, for an LCA study with the goal of comparing different production routes for the same product, a common simplification is to reduce the system boundary to cradle-to-gate (see Fig. 1). A cradle-to-gate system boundary considers all upstream processes and neglects identical downstream processes after manufacturing of the product, such as identical use phases or identical end-of-life treatments.[28] In this study, we use a cradle-to-gate system boundary for LCA environmental impacts to align with the intended application of the mass intensity, *i.e.*, comparing different production routes.

We calculate the LCA environmental impacts for producing 1 kg of the final chemical. For environmental impact selection, there exists a variety of environmental impacts, which are typically collectively assessed in one life-cycle impact assessment (LCIA) method. The European Commission's Joint Research Centre provides a collection of recommended environmental impacts in the LCIA method "Environmental Footprint 3.0". To follow this recommendation, we use "Environmental Footprint 3.0" as our LCIA method.[29] In our study, the cradle-to-gate LCA environmental impacts are the benchmark for evaluating the mass intensities with eight different system boundaries (see section 2.3).

2.2 Mass intensities in "green chemistry"

In "green chemistry evaluations", various mass-based metrics have been introduced as indicators to capture the environmental performance of chemical processes. One of the first mass-based GCMs was the Environmental Factor (*E*-Factor), introduced by Roger Sheldon.[14,30] The *E*-factor measures the amount of waste produced per kilogram of the final chemical product. As a definition of waste, Roger Sheldon considers anything that is not the desired product.[14,30] This broad definition also includes indirect wastes, *e.g.*, carbon dioxide (CO_2) emissions released during the energy supply for chemical processes.[21] However, Sheldon acknowledges the practical challenge of accounting for energy demand due to data availability.[21] Furthermore, the *E*-factor originally had a gate-to-gate system boundary, *i.e.*, calculation started with raw materials entering the factory and ended with obtaining the final product. However, Sheldon noted that waste production from intermediates should be included in the *E*-factor calculation, and that commonly available materials could serve as a starting point.[21]

While the *E*-factor focuses on the amount of waste produced by chemical production (which is an output perspective), another approach for environmental assessment of chemical processes is to focus on the materials used in the process (which uses an input perspective). Of course, both approaches are interrelated by the law of conservation of mass. The latter approach led to the development of mass intensity metrics like the Process Mass Intensity (PMI). According to the ACS GCI pharmaceutical roundtable the "*PMI accounts for all materials used within a pharmaceutical process, including reactants, reagents, solvents (used in the reaction and purification), and catalysts*" per kilogram final chemical product.[31] In the past decade, the PMI was promoted by GSK and the ACS GCI pharmaceutical roundtable as a key metric for evaluating environmental performance.[18,21]

Despite its widespread adoption, the scope of the PMI is ambiguously defined in scientific literature in two distinct dimensions, to which we refer as vertical and horizontal dimensions (see Fig. 1). The 'vertical' dimension refers to the extent to which materials are included in PMI calculation within a specific production site (*e.g.*, materials used in synthesis, product isolation and purification, equipment cleaning and conditioning, and energy-supply processes). The 'horizontal' dimension refers to the extent to which upstream processes are included in PMI calculation (*e.g.*, gate-to-gate, 'commonly available materials'-to-gate, or cradle-to-gate).

With regard to the 'vertical' expansion of the PMI scope, it is often unclear whether auxiliaries for cleaning (*e.g.*, additional solvents consumption) and for energy supply (*e.g.*, natural gas) are included in the scope of the PMI. Typically, the PMI does not consider material use for equipment cleaning and conditioning, which can contribute significantly to the mass intensity, especially of Active Pharmaceutical Ingredients (API).[32] Some literature specifically limit the PMI only to the materials fed into the chemical synthesis process and subsequent isolation and purification steps, and thus excludes auxiliary materials.[13] However, the inclusion of CO_2 in the *E*-factor[21] suggests that the PMI should also consider materials used in energy provision to maintain alignment with the often-quoted relationship (PMI = *E*-factor + 1),[20] further highlighting the ambiguous definition of PMI's scope.

Considering the 'horizontal' expansion, the original focus of PMI was solely on the material inputs of a specific production site (gate-to-gate), similar to the original definition of the *E*-factor. However, recognizing the importance of value chain impacts, the scientific community has advocated for a broader scope, starting from 'commonly available materials'.[18,24] Yet, the PMI is often calculated using a gate-to-gate system boundary for practical reasons.

To analyze the current practical application of the PMI, we define the system boundary on a gate-to-gate basis, representing the horizontal degree of integration. Furthermore, for the vertical degree of integration, we include all materials entering the producer's specific production site to produce one kilogram of the final product; thus, auxiliary materials are included in the PMI calculation.

2.3 System boundaries for calculation of mass intensities

The mass intensity using a gate-to-gate system boundary is referred to as PMI (see section 2.2), while those with a cradle-to-gate system boundary are termed Value Chain Mass Intensity (VCMI) in this study. Notably, while the PMI can include the amount of intermediates used in a process, such as chemical intermediates or solvents, the VCMI considers the natural resources required to produce these intermediates, such as crude oil or metal ores, due to its cradle-to-gate system boundary (see Fig. 1). Similar to LCA, the VCMI considers all mass expenditures of the entire upstream value chain including resources used for the production of chemicals as well as any resources from upstream intermediates that are typically not considered in PMI calculations, *e.g.*, resources for electricity supply (coal, natural gas, *etc.*) (see Fig. 1).

All substances in the system boundary are considered for both the PMI and the VCMI calculations, *i.e.*, water is also included.[18] However, chemical processes often consume large amounts of water and at the same time, the environmental impact of the water supply is relatively low.[17,33] Intensive water use of chemical processes combined with the relatively low environmental impacts of water supply may reduce the strength of the correlation between the PMI and the VCMI and LCA environmental impacts.[17] Therefore, two cases for the calculation of the PMI and the VCMI are considered here: including water (PMI_{inw} and $VCMI_{inw}$) and excluding water (PMI_{exw} and $VCMI_{exw}$).

Furthermore, to reduce the effort for data collection for VCMI calculation, we aim to identify the most important product classes that have the highest impact on the environmental performance of chemical production. For this purpose, we categorize all value chain products in the LCA database ecoinvent into seven groups, using the Central Product Classification (CPC) of the United Nations (see Table 1).[27]

Table 1 CPC product classification classes used for the value chain products of ecoinvent[27]

Product class (abbreviation)	CPC classification
Chemicals (Chem)	• Basic organic chemicals • Basic inorganic chemicals • Other chemical products • Miscellaneous basic chemical products
Refined fossil raw materials energy carrier (Fos)	• Crude petroleum and natural gas • Petroleum oils and oils obtained from bituminous materials • Hard coal • Brown coal • Petroleum gases and other gaseous hydrocarbons, except natural gas
Energy (Ene)	• Steam and hot water • Electrical energy
Minerals and metals (MM)	• Basic metals • Copper, nickel, aluminum, alumina, lead, zinc, tin, and unwrought • Metal ores • Metal wastes or scraps • Other non-ferrous metals and articles thereof (including waste and scrap of some metals) • Chemical and fertilizer minerals
Biomass feedstocks (Bio)	• Vegetable oils • Products of agriculture, horticulture and market gardening cereals • Forestry and logging products wood in the rough • Veneer sheets, sheets for plywood, densified wood • Fertilizers and pesticides • Oilseeds and oleaginous fruits
Water (H_2O)	• Natural water
Other (Oth)	• All other products

Subsequently, we expand the system boundary stepwise by successively adding the corresponding processes for the product classes from Table 1 to the VCMI system boundary. We then calculate the resulting VCMI for each expanded system boundary and analyze the impact of product classes on the correlation between the VCMI and LCA environmental impacts.

For clarification, while a product class contains multiple intermediate products – such as chemical intermediates, heat or electricity – the VCMI considers the natural resources required for the production of these products due to VCMI's cradle-to-gate system boundary. In other words, adding product classes to the system boundary increases the VCMI by accounting for the additional natural resources that are required to produce the products in that product class (see Fig. 2). Therefore, while most of the chemicals we investigated are still fossil-based, the amount of fossil feedstock and fossil energy required for their production, such as crude oil or natural gas, are only considered in the VCMI if the product class labeled '*refined fossil raw materials and energy carriers*' ('Fos') is included in the VCMI system boundary (see Table 1).

The degree to which the correlation strengthens by including a product class in the system boundary indicates the importance of the respective product class for VCMI calculation. Fig. 2 provides a schematic representation of the meth-

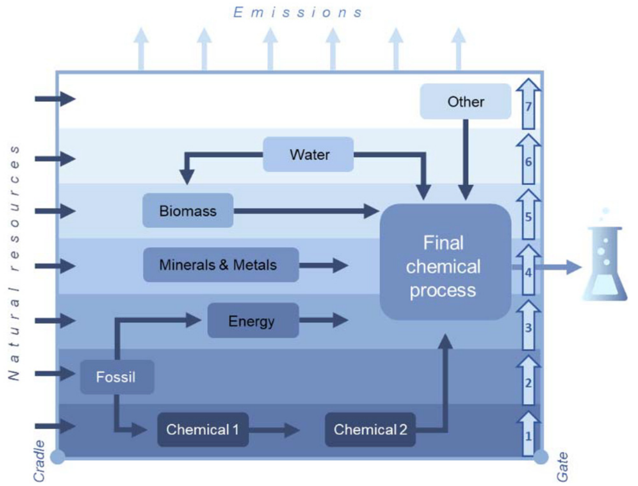

Fig. 2 Simplified example of the seven VCMI cradle-to-gate system boundaries. The blue arrows illustrate the stepwise system boundary expansion.

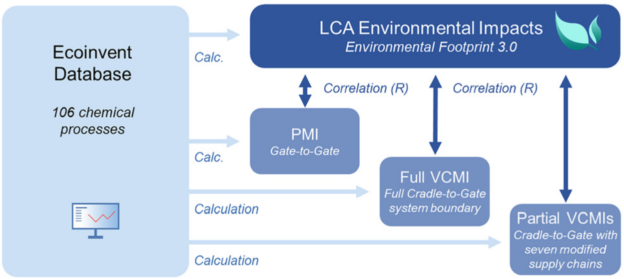

Fig. 3 Schematic overview of the methodology.

odology employed for the stepwise inclusion of the value chain products for VCMI calculation. The figure illustrates the seven distinct product classes from Table 1, stacked from bottom (1) to top (7). This stacking represents the order in which these classes are incorporated into the VCMI calculation. Importantly, the results of section 3 are sensitive to the order in which the product classes are included in the system boundary. In this study, we included the product classes to achieve the highest correlation for '*climate change impact*' with as few product class expansions as possible (see section 3).

We use chemical datasets from the ecoinvent LCA database version 3.8 for PMI, VCMIs and LCA environmental impact calculation.[26] Each chemical dataset represents the production of a specific chemical. These datasets provide information on the production process of the chemicals, including mass input, emissions, and energy demand, as well as insights into the corresponding value chain. To ensure consistency, we selected chemical processes according to criteria detailed in the ESI,† resulting in the use of 106 chemical datasets for the correlation analysis; specifically, we excluded datasets which are based on the use of heuristics and thus leads to poor data quality. The selected datasets are used for calculating the (gate-to-gate) PMI, the (full) VCMI considering the entire cradle-to-gate system boundary with all product classes, the (partial) VCMIs with seven modified cradle-to-gate system boundaries (some product classes excluded, as described in this section), and the LCA environmental impacts (see Fig. 3). We used the open-source Python package Brightway for these calculations.[34]

An important process for the chemical industry is the naphtha steam cracking process.[35] The ecoinvent dataset for the naphtha steam cracking process is a so-called aggregated process, *i.e.*, the process and the associated value chain are combined into one dataset.[34] Due to the aggregation of the naphtha steam-cracking dataset, it is not possible to perform a stepwise expansion of the value chain. Therefore, we modeled the steam-cracking process and replaced the ecoinvent steam-cracking process with our own model of a steam-cracking process within the chemical value chain. A detailed description of the steam cracking process modeling can be found in the ESI.†

2.4 Correlation analysis

In this study we systematically analyze whether and with which system boundaries mass intensities can serve as a measure to capture LCA environmental impacts, *i.e.*, whether and when there is a correlation between the Process Mass Intensity (PMI) or the Value Chain Mass Intensity (VCMI) and LCA environmental impacts, and how strong this correlation is.

To analyze the correlation between the mass intensities (PMI/VCMI) and LCA environmental impacts, we use the Spearman (rank) correlation coefficient (R), since it is less restrictive than other correlation coefficients. The Spearman correlation can be used to analyze the strength of any monotonically increasing or decreasing correlation. In other words, it measures how consistently one variable increases or decreases as the other variable changes, thus providing a quantitative evaluation of qualitative trends. Other correlation coefficients, *e.g.*, the Pearson correlation coefficient, can only be used to evaluate the strength of specific correlations, like linear correlations.[27] However, we also include results for Pearson correlation coefficient in the ESI.†

The Spearman correlation coefficient R ranges from -1 to $+1$.[36]

- An R-value of $+1$ describes a perfect positive correlation, *i.e.*, increasing one variable always increases the second variable.[36]
- An R-value of -1 describes a perfect negative correlation, *i.e.*, increasing one variable always decreases the second variable.[36]
- An R-value of 0 means no correlation between the two parameters.[36]

The higher the absolute value of the Spearman correlation coefficient, the stronger the correlation, which indicates that the considered mass intensity may serve as a proxy for LCA environmental impacts. However, if the Spearman correlation coefficient is low, the considered mass intensity is probably no reliable proxy for LCA environmental impacts. It is noteworthy that the interpretation of correlation coefficients varies widely in different scientific research fields. There is no commonly agreed rule for interpreting the strength of the correlation.[36] In our study, we interpret the correlation coefficient R according to the definitions in Table 2.[37]

Besides the strength of the correlation, the statistical significance of correlation coefficient should also be reported.[36] The statistical significance is quantified by the p-value, which reflects the probability that the measured correlation coefficient is due to chance. If the p-value is below a predefined significance level α, the measured correlation coefficient is considered statistically significant.[38] In this study, we choose a significance level of 5%, *i.e.*, $\alpha = 0.05$, which is a commonly used significance level.[38,39]

3 Results and discussion

This section presents the results of the correlation analyses outlined in section 2. To investigate the influence of a gate-to-gate *vs.* a cradle-to-gate system boundary, we evaluate the Spearman correlation coefficients between the LCA environmental impacts and both the PMI and the full VCMI (including all product classes of Table 1) in section 3.1. In section 3.2 we then evaluate the Spearman correlation coefficients between LCA environmental impacts and the partial VCMIs with seven modified system boundaries (*i.e.*, different sets of product classes considered), to analyze the effect of product classes on the strength of the correlation. In section 3.3, we then identify the key influencing resources (*i.e.*, input materials entering the cradle-to-gate system boundary of the VCMI) driving the strength of the correlation with environmental impacts. Through a detailed discussion of these correlations for specific environmental impacts in section 3.4, we explore the causal relationships between resource consumption considered in the full VCMI and these environmental impacts, highlighting critical considerations for using mass intensities as proxies.

3.1 Comparison between (gate-to-gate) PMI and full (cradle-to-gate) VCMI

Fig. 4 shows the Spearman correlation coefficients between the LCA environmental impacts and the PMI_{exw} and the full VCMI_{exw} (both excluding water). The Spearman correlation coefficients between the PMI_{inw} and the full VCMI_{inw} and the LCA environmental impacts can be found in the ESI.† Excluding water from the PMI and the full VCMI calculations results in higher Spearman correlation coefficients for thirteen and twelve out of sixteen LCA environmental impacts, respectively. The p-values of all the correlation coefficients presented in Fig. 4 are below the predefined significance level of 5% (see section 2.4), indicating that these results are statistically significant (see ESI†). In the following, we will discuss the overall strength of correlation for the PMI and the full VCMI, respectively.

In Fig. 4, all Spearman correlation coefficients are positive, which means that a higher PMI and full VCMI indicate higher LCA environmental impacts. For the PMI, the correlation is weak or very weak for thirteen and for three out of sixteen LCA environmental impacts, respectively. This mostly very weak correlation between the PMI and LCA environmental impacts suggests that a gate-to-gate PMI is inappropriate for approximating LCA environmental impacts, further reinforcing the findings of a previous study.[23]

The Spearman correlation coefficient significantly improves for fifteen out of sixteen LCA environmental impacts when the full VCMI was used instead of the PMI. In contrast to the PMI, the Spearman correlation coefficient between the full VCMI and the LCA environmental impacts, is strong for ten, moderate for five, and very weak for one out of sixteen LCA environmental impacts. A very weak correlation between the full VCMI and LCA is observed for ozone depletion impact. For this environmental impact, the correlation for both the PMI and the full VCMI is weak or very weak, respectively, indicating that ozone depletion impact cannot be represented by the mass-based metrics PMI or full VCMI. An explanation for the very weak correlation is provided in section 3.4.

Our results show that the correlations between the full VCMI and the LCA environmental impacts are significantly stronger than the correlations between the PMI and the LCA environmental impacts. The significantly higher correlation for the full VCMI demonstrates that using a cradle-to-gate system boundary instead of a gate-to-gate system boundary can substantially improve the correlation between mass intensities and most environmental impacts.

However, extending the system boundary, as applied in the full VCMI, also demands considerably greater data collection effort. Even though the full VCMI requires less data than a complete LCA study (since only resource consumption data is needed and not emissions of processes), the calculation of the full VCMI can still be laborious. Challenges in acquiring data for the full VCMI are similar to those encountered in LCA, as discussed in the introduction. These challenges include data confidentiality and the time and cost of data collection. Thus, simplifying data acquisition could be beneficial by focusing data collection efforts on the most important products rather than the entire value chain. To explore this potential simplification and its effect on correlation coefficients, we analyzed how including product classes in the VCMI system boundary impacts these correlations.

Table 2 Interpretation of correlation coefficient (R)[37]

Correlation coefficient (R)	Interpretation
$0.9 \le \lvert R \rvert \le 1.0$	Very strong correlation
$0.7 \le \lvert R \rvert < 0.9$	Strong correlation
$0.5 \le \lvert R \rvert < 0.7$	Moderate correlation
$0.3 \le \lvert R \rvert < 0.5$	Weak correlation
$0.0 \le \lvert R \rvert < 0.3$	Very weak, if any correlation

3.2 Influence of product class inclusion in VCMI

To better understand the influence of different product classes, we divide the entire upstream value chain into seven classes. We then gradually expand the cradle-to-gate system

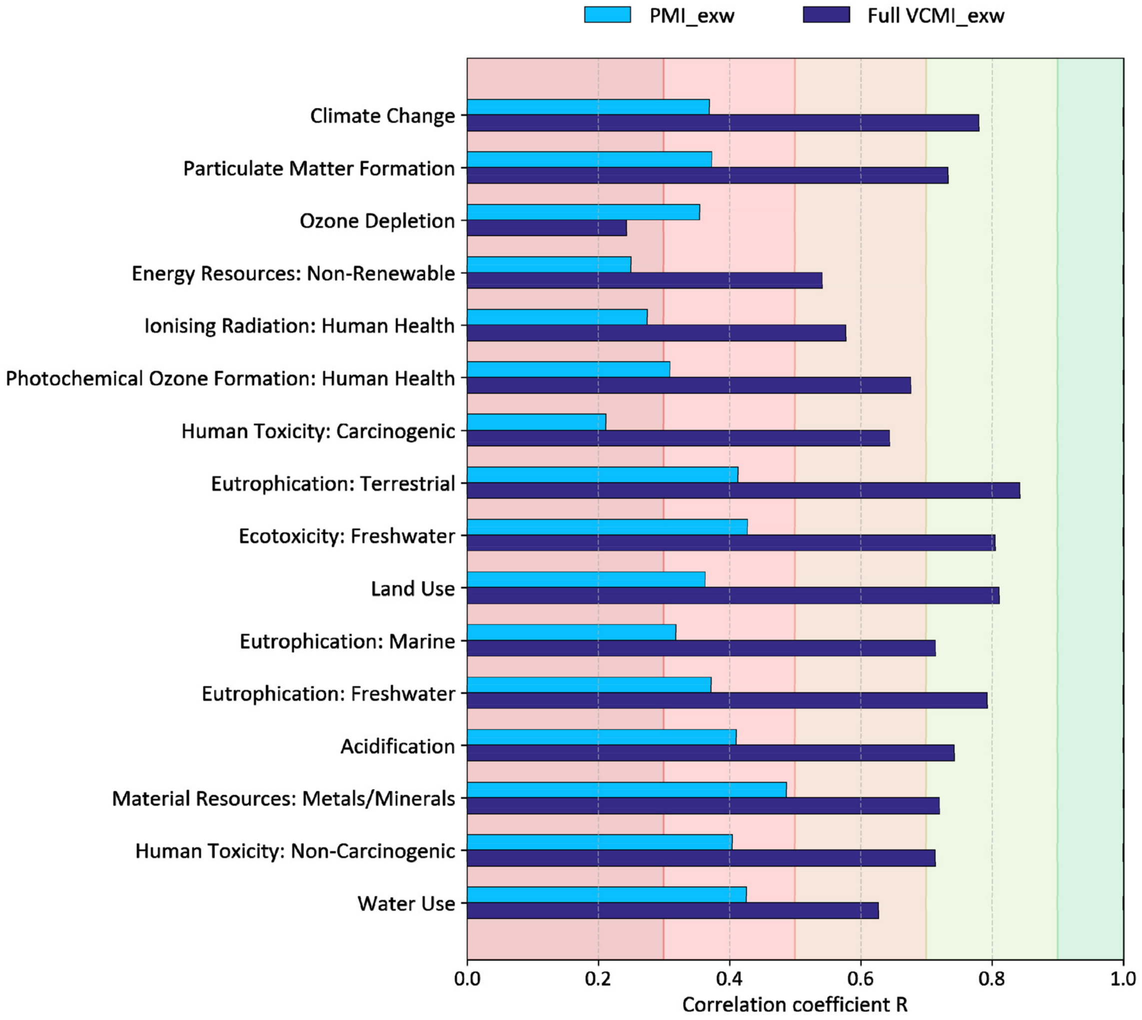

Fig. 4 Correlation coefficient between PMI or full VCMI and environmental impacts from LCA for 106 chemicals. The full VCMI contains the mass expenditure of the entire cradle-to-gate system boundary, *i.e.*, all product classes of the value chain are included in the system boundary. The background colors correspond to the interpretation classification of the correlation coefficient defined in Table 1.

boundary by incorporating the processes required for each product class in the entire value chain (see Fig. 2). This stepwise approach yields seven different system boundaries for the VCMI calculation (see section 2.3).

In particular, we analyze the influence of system boundary expansion by product class inclusion on the correlation coefficients for four LCA environmental impacts: '*climate change* impact', '*ozone depletion impact*', '*particulate matter formation*', and '*energy resource: non renewable*'. The first three environmental impacts were selected due to their high reliability in modeling environmental burdens, as emphasized by the European Commission's Joint Research Centre.[40] However, these three environmental impacts are exclusively emission-based, *i.e.*, focus on process outputs (emissions generated). In contrast, resource-based environmental impacts focus on process inputs (resources required). Since mass intensities are inherently resource-based, we further add the environmental impact '*energy resource: non-renewable*' in this analysis, enabling a comparison between emission-based and resource-based environmental impacts (see section 3.4). In addition to these four LCA environmental impacts, we provide the Spearman correlation coefficients for all sixteen LCA environmental impacts in the ESI.†

Fig. 5a presents the correlation coefficients between the four environmental impacts and the VCMIs with seven varied system boundaries, allowing two significant observations: first, each system boundary expansion step affects the correlation differently, either increasing or decreasing it. For example, when looking at '*climate change impact*', including '*energy*' ("Ene") strengthens the correlation, whereas including '*minerals and metals*' ("MM") weakens it. This varying influence on the correlation suggests that product classes are of different importance for the VCMI calculation when it is used as a proxy for environmental impacts.

Second, the effect of these product classes on the strength of the correlation is not consistent across the environmental

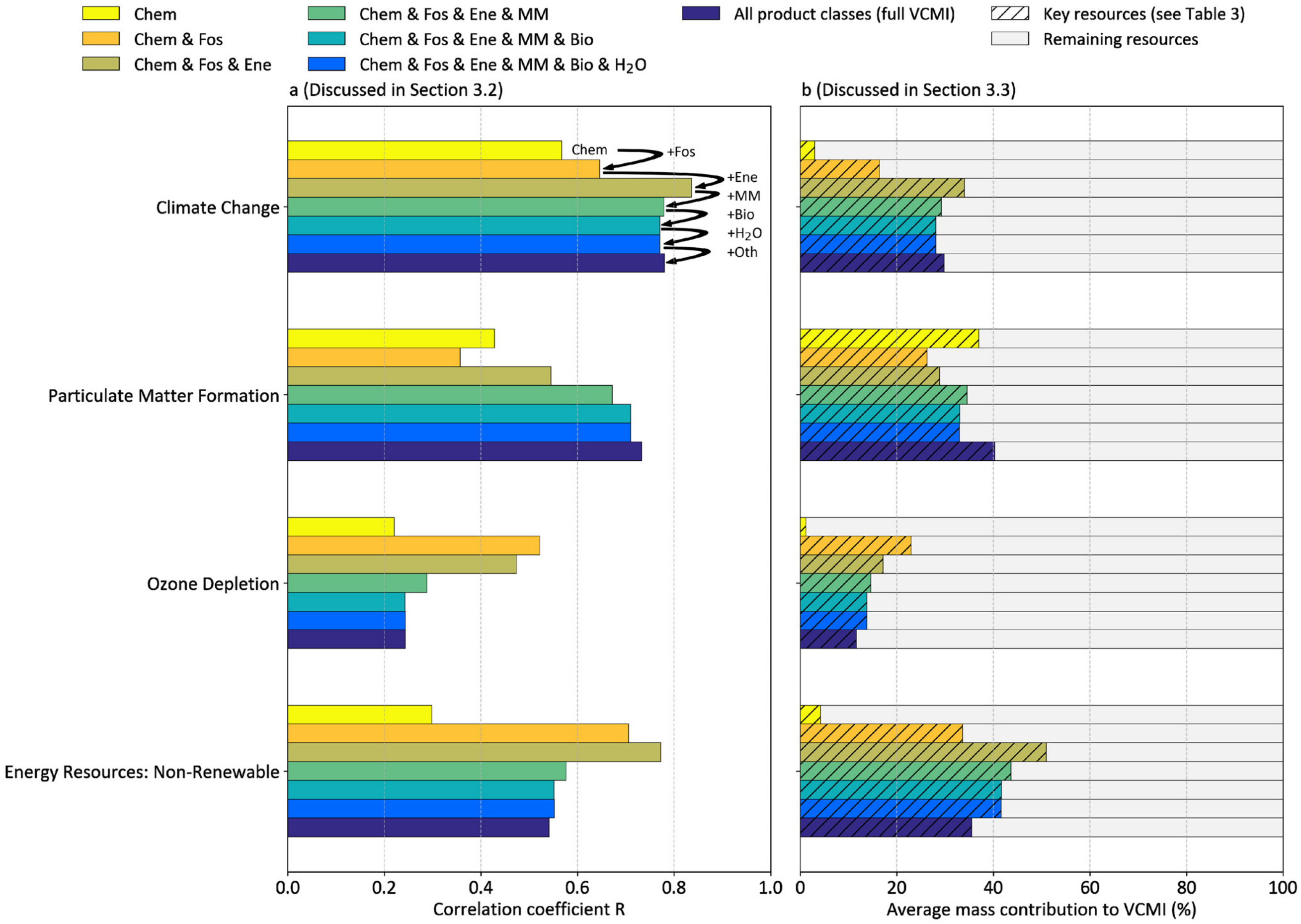

Fig. 5 Correlation coefficients between the VCMI with modified system boundaries and the recommended environmental impacts: climate change, particulate matter formation, and ozone depletion. Additionally, energy resource: non-renewable was included to introduce resource-based environmental impacts into the analysis.

impacts. Including some product classes in the VCMI system boundary may even decrease the correlation coefficient between the VCMI and certain environmental impacts, while improving the correlation for others. For instance, when processes for '*refined fossil raw materials and energy carriers*' ("Fos") are included, the correlation with '*climate change impact*' strengthens, but the correlation with '*particulate matter formation*' becomes weaker. The varying effect across environmental impacts demonstrates that the relevance of product classes depends on the specific environmental impact. Furthermore, this variability highlights that a single metric with a fixed system boundary cannot adequately reflect the inherently multi-criteria nature of environmental sustainability.

While neither the full VCMI nor the partial VCMIs are suitable as a universal metric for environmental sustainability assessment, the varying influence of system boundary expansions shown in Fig. 5a suggests that a VCMI specifically tailored to individual environmental impacts could still potentially serve as a proxy for these impacts. However, tailoring the VCMI requires a deeper understanding of why stepwise system boundary expansions disproportionately affect environmental impacts. To explore these dynamics, we disaggregated the full VCMI into its individual components (resources) and analyzed each resource separately. In particular, we examined the correlation between each individual resource and environmental impacts to identify the key resources that improve the strength of these correlations the most. This analysis provides deeper insights into the causal relationship between resource demand, as reflected by the VCMI, and environmental impacts. Furthermore, the inferred causal relationships between resource demand and environmental impacts highlight critical considerations for using mass intensities in general as proxies for environmental impacts. Section 3.3 identifies the key resources driving the correlations, while section 3.4 discusses their causal relationships with the four selected environmental impacts in detail.

3.3 Identification of key resources driving the strength of correlations

This section aims at analyzing the influence of individual resources on the strength of correlations with environmental impacts. Due to the high number of possible resources that the VCMI can include (up to 126), a comprehensive interpretation of each resource is not practical. Therefore, we first identify the key resources driving the strength of correlations between the full VCMI (including all product classes) and environmental impacts. As in section 3.2, we use the environmental impacts '*climate change* impact', '*ozone depletion* impact', '*particulate matter formation*', and '*energy resource: non renewable*' as examples here. Subsequently, in section 3.4, we will discuss the causal relationships between these key resources and the four selected environmental impacts in detail.

For the interpretation of the individual environmental impacts in section 3.4, we distinguish between resources that directly or indirectly influence environmental impacts (see Fig. 6). Emission-based environmental impacts can only be influenced indirectly through resource-based indicators such as the VCMI. For example, coal input into a process does not directly contribute to '*climate change impact*'; instead, coal combustion transforms the carbon content of coal into CO_2, which contributes to '*climate change impact*' if it is released into the atmosphere. Thus, the coal combustion process links the input perspective of the VCMI (*i.e.* resources used) to the output perspective of emission-based impacts (*i.e.* emissions released to the environment). Further discussion of the implications of emission-based environmental impacts is provided in section 3.4. In contrast to emission-based environmental impacts, resource-based environmental impacts are calculated directly from the resource consumption data collected in the VCMI. For instance, the same coal input considered in the VCMI directly contributes to the resource-based environmental impact '*energy resource: non-renewable*'.

Each point in Fig. 6 represents the correlation coefficient of an individual resource within the full VCMI and its corresponding average mass contribution. This representation allows for the separate analysis of each resource within the full VCMI. Resources with a strong correlation and high mass contribution have the highest positive influence on the overall correlation between the full VCMI and the corresponding environmental impact. Conversely, resources with a weak correlation and high mass contribution negatively affect the overall corre-

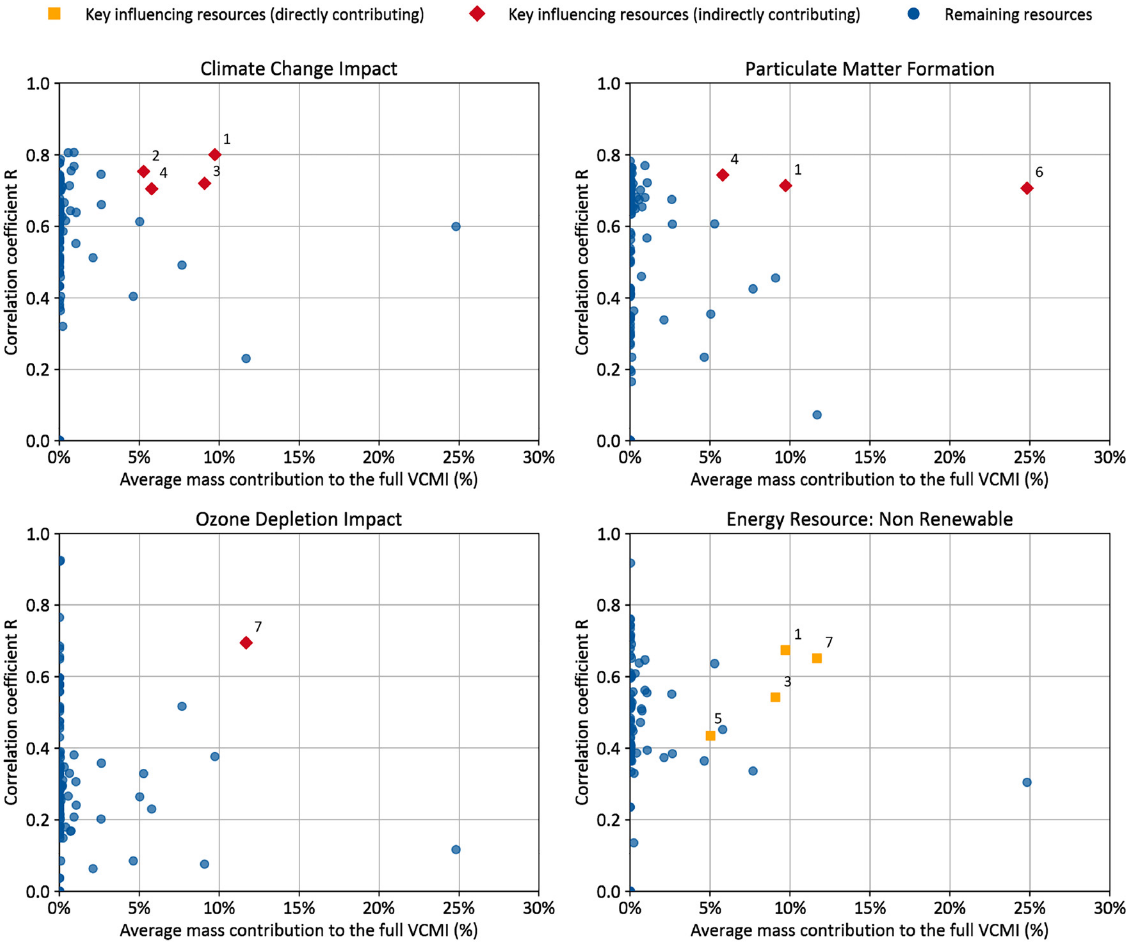

Fig. 6 Analysis of the correlation of each resource (126 resources) in the full VCMI with LCA environmental impacts for 106 chemicals. Each point represents a single resource in the full VCMI. Diamonds and squares in the figure highlight the key resources for each environmental impact, based on their correlation coefficient and average mass contribution to the full VCMI (including all product classes). Detailed information about these resources is provided in Table 3.

lation. However, the majority of resources show very low mass contributions to the full VCMI. For example, more than half of the resources show an average mass contribution of less than 0.01%. Resources with such low mass contributions have minimal impact on the full VCMI and therefore contribute negligibly to the correlation between the full VCMI and environmental impacts.

In this study, we defined key resources that serve as indicators for environmental impacts as those that exhibit an average mass contribution of at least 5% to the VCMI and either (i) strongly correlate ($R \geq 0.7$) with the corresponding environmental impact (red diamonds in Fig. 6) or (ii) directly contribute to the respective environmental impact (yellow squares in Fig. 6). In sum, seven key resources were identified for the four considered environmental impacts. Detailed information about these key resources is provided in Table 3.

To assess the significance of the identified key resources, we compared their share of the full VCMI with the correlation coefficient in Fig. 5. Fig. 5b illustrates the share of key resources, while Fig. 5a depicts the correlation coefficient as product classes are progressively included in the VCMI system boundary. A comparison of both figures reveals that the correlation coefficient trend closely aligns with the trend of the share of key resources within the VCMI. This alignment suggests that the correlation between the VCMI and environmental impacts depends on only a few resources (up to a maximum of four), which vary depending on the specific environmental impact considered. The finding that each environmental impact is approximated by a different set of key resources further highlights the challenges of capturing the multi-criteria nature of environmental sustainability with a single metric.

3.4 Causal relationships between resource uptake and environmental impacts

In this section, we analyze the causal relationship between the key resources identified in section 3.3 and the four considered environmental impacts. With this analysis we investigate why these resources serve as indicators for their respective environmental impacts and offer critical insights into the use of mass intensities for environmental assessment.

3.4.1 Climate change impact. *'Climate change impact'* serves as an indicator for global climate change caused by GHG emissions such as CO_2, methane and nitrous oxide.[29]

Fig. 5a shows that including processes for *'chemicals'*, *'refined fossil raw materials and energy carriers'*, and *'energy'* conversion in the VCMI system boundary significantly strengthen the correlation between the VCMI and '*climate change impact*'. This significant improvement is largely due to the consumption of fossil resources – such as coal and natural gas – in the corresponding processes. These fossil resources are either used as feedstock or energy source. When used as an energy source, these fossil resources are converted into CO_2 *via* combustion, which contributes to '*climate change impact*' when the CO_2 is emitted into the atmosphere. The conversion of fossil resources to CO_2 explains the strong correlation of the resources "Coal, hard" and "Gas, natural" with '*climate change impact*' (see Table 3) for the datasets used in this study. In addition to coal and natural gas, Table 3 shows that "Shale" and "Gravel" can also serve as indicators of '*climate change impact*'. To better understand the strong correlation of shale and gravel, we analyzed the processes consuming these two resources within the chemical value chain of the 106 chemical processes.

In these value chains, shale is typically a byproduct of fossil resource extraction. Therefore, higher shale extraction signals higher fossil resource consumption, leading to increased GHG-emissions, which explains shale's strong correlation with '*climate change impact*'. On the other hand, gravel is primarily used to construct railways that transport coal for the chemical value chain. Consequently, higher gravel consumption implies higher coal transportation and, in turn, higher GHG-emissions, resulting in a strong correlation for gravel. These examples clearly demonstrates that the relationship between a consumed resource and its '*climate change impact*' can vary in complexity. While some resources, like coal and natural gas, are converted to emissions, others, like shale and gravel, exhibit more complex relationships. Yet, these key resources (coal, natural gas, shale, and gravel) serve as indirect indicators of '*climate change impact*', as the consumption of these resources only implies processes within the value chain. For example, coal consumption implies coal combustion, which generates CO_2 emissions if it is released into the atmosphere, making coal a key resource for approximating '*climate change impact*'. This example illustrates that the resource-based approximation of emission-based environmental impacts, such as '*climate change impact*', requires processes that connect the input perspective of the VCMI (resources used)

Table 3 Key resources for the correlation between the full VCMI and environmental impacts. A star (*) indicates that the resource is relevant for the respective environmental impact

No. in Fig. 6	Resource	Avarage mass	Climate change Spearman *R*	Particulate matter formation Spearman *R*	Ozone depletion Spearman *R*	Energy resource Spearman *R*
1	Coal, hard	9.7%	0.80*	0.71*	0.38	0.67*
2	Shale	5.3%	0.75*	0.61	0.33	0.64
3	Gas, natural	9.1%	0.72*	0.46	0.07	0.54*
4	Gravel	5.8%	0.70*	0.74*	0.23	0.45
5	Coal, brown	5.0%	0.61	0.36	0.26	0.43*
6	Gangue	24.8%	0.60	0.71*	0.12	0.30
7	Oil, crude	11.7%	0.23	0.07	0.70*	0.65*

with the output perspective of emission-based environmental impacts (emissions released to the environment).

However, using resources to approximate emission-based environmental impacts is problematic, as the reliability of resources to serve as proxies strongly depends on technologies established in the value chain, which may change in the future. For example, implementing carbon capture and storage (CCS) at coal-based power plants could significantly diminish the strength of the correlation between coal consumption and '*climate change impact*'. Although future technological developments were not investigated in this study, this finding underscores the importance of focusing on environmental impacts directly, rather than relying solely on metrics to approximate them. The use of some metrics as proxy can lose meaning over time as technologies and value chains evolve, while the environmental impacts themselves remain meaningful and consistent, even with temporal changes. This highlights the significance of LCA as a consistent framework, since it allows for the accounting of technological changes.

Strikingly, the resource "Oil, crude" shows only a weak correlation with '*climate change impact*' (see Table 3). To investigate this, we again analyzed the oil-consuming processes within the chemical value chain. In this context, crude oil is primarily used as a fossil feedstock rather than an energy carrier. Processes that utilize crude oil as a chemical feedstock are designed to efficiently convert its carbon into value-added chemicals, resulting in relatively minor direct CO_2 emissions during chemical production compared to those generated from energy conversion. It should be noted that, due to the cradle-to-gate system boundary considered in this study, CO_2 emissions generated during the end-of-life phase through incineration of the used value products are not accounted for. In a cradle-to-grave analysis, the resulting correlation would likely be stronger.

Including the remaining four product classes, *i.e.*, '*minerals and metals*', '*biomass feedstocks*', '*water*', and '*other*' products in the system boundary weakens the strength of the correlation between the VCMI and '*climate change impact*'. The weaker correlation is likely because the consumption of the resources required for these products generates less GHG-emissions compared to the consumption of fossil resources, thus weakening the correlation between the VCMI and the '*climate change impact*'. This is also reflected in the share of key resources in Fig. 5b, which decreases slightly.

3.4.2 Particulate matter formation.

'*Particulate matter formation*' refers to the health effects of airborne particles, which can cause respiratory issues as a result of emissions, such as particles with a diameter of 2.5 micrometers or smaller, nitrogen oxides, and sulfur oxides.[41]

Looking at Fig. 5a, the correlation coefficient decreases when '*refined fossil raw materials and energy carriers*' are included in the VCMI system boundary. However, the inclusion of the other five product classes, *i.e.*, '*energy*', '*minerals and metals*', '*biomass feedstocks*', '*water*', and '*other*', increases the correlation coefficient. To explain the trend in the Spearman correlation coefficient, we examined which processes contribute most to '*particulate matter formation*' across the 106 chemical value chains. In the chemical value chains, energy conversion of coal and the production of inorganic sulfur-containing chemicals, such as sulfur dioxide and sulfuric acid, are the major contributors to '*particulate matter formation*'. This finding explains why coal is a key resource for indicating '*particulate matter formation*' in the VCMI (see Table 3), as well as gravel, which supports the transportation of coal (see section 3.4.1). Similarly, the production of inorganic sulfur-containing chemicals is associated with the formation of sulfur trioxide aerosols. These aerosols contribute to '*particulate matter formation*' if emission reduction systems are not installed. Consequently, higher resource consumption related to sulfur-containing chemicals indicates higher '*particulate matter formation*'.

Keeping this in mind, the development of the correlation coefficient in Fig. 5a can be interpreted as follows. The correlation coefficient decreases with including '*refined fossil raw materials and energy carriers*'. Even though this inclusion increases the total mass of fossil resources, in this specific system boundary – where only '*chemicals*' and '*refined fossil raw materials and energy carriers*' are considered – fossil resources are primarily used as feedstock for chemical reactions (mainly crude oil) rather than for energy conversion. Notably, unlike burning coal for energy conversion, using fossil resources as feedstock for chemical reactions does not directly contribute to '*particulate matter formation*'. Therefore, the inclusion of resource consumption, which is not directly linked to '*particulate matter formation*', explains the observed decrease in the Spearman correlation coefficient when '*refined fossil raw materials and energy carriers*' are included in the system boundary. However, including '*energy*' conversion strengthens the correlation, which can be attributed to the current reliance on coal combustion for energy supply.

Including '*minerals and metals*' further strengthens the correlation, as the consumption of ores like copper sulfide increases. These ores are essential for general construction activities, such as transmission network development, and for sulfur production. Both activities are indirectly linked to '*particulate matter formation*': increased transmission network requirements indicate higher electricity demand and, consequently, greater coal combustion. Similarly, higher sulfur production leads to higher emissions of sulfur oxide aerosols, contributing to higher '*particulate matter formation*' as described earlier in this section. The connection between ore consumption and '*particulate matter formation*' explains why "Gangue" serves as an indicator for '*particulate matter formation*'. Gangue is a waste material commonly extracted alongside the desired ores, such as copper sulfide, during mining activities.

It should be noted, however, that the relation between energy demand, gangue and '*particulate matter formation*' is a typical spurious correlation. This correlation would likely weaken if energy supply were based on non-particulate-matter-emitting sources and circular economy approaches for desired metals were established. This again shows that the observed correlations between VCMI and environmental impacts are sensitive to future changes in the supply chain, particularly shifts towards cleaner energy sources and circular economy in the case of '*particulate matter formation*'. Thus, the '*particulate matter formation*' example again underscores the need to consider environmental impacts directly, as the relevance of a single metric can diminish over time, while the environmental impact itself remains meaningful even with temporal changes.

The stepwise inclusion of the other product classes ('*biomass feedstocks*', '*water*', and '*other*') in the VCMI system boundary further improves the strength of this correlation since the energy demand of these partial value chains gradually converges to the actual energy demand of the entire value chain.

3.4.3 Ozone depletion impact. '*Ozone depletion impact*' represents the emissions of ozone-depleting substances, which contribute to the reduction of the ozone layer, resulting in increased ultraviolet radiation reaching the Earth's surface.[41] Key ozone-depleting emissions include chlorofluorocarbons, hydrochlorofluorocarbons, and Halons (*e.g.* Halon 1301).[42]

Fig. 5a shows a stronger correlation between the VCMI and '*ozone depletion impact*' when '*refined fossil raw materials and energy carriers*' are integrated into the VCMI system boundary. However, the correlation coefficient decreases with the other five system boundary expansion steps ('*energy*', '*minerals and metals*', '*biomass feedstocks*', '*water*', and '*other*'). Examining the processes that contribute to '*ozone depletion impact*' in the 106 chemical value chains reveals that crude oil extraction plays a significant role, primarily due to the potential use of Halon 1301. Halon 1301 is a fluorinated hydrocarbon that is allowed only for specific applications such as fire extinguishers within the oil and gas industry.[43] Therefore, higher crude oil consumption signals increased '*ozone depletion impacts*', explaining the role of "Oil, crude" as a key resource for indicating '*ozone depletion impact*', as shown in Table 3. Therefore, when '*refined fossil raw materials and energy carriers*' are included in the VCMI system boundary, the key resource crude oil is captured in the VCMI, which improves the correlation between the VCMI and '*ozone depletion impact*' (see Fig. 5a).

However, it's crucial to acknowledge that under the Montreal Protocol's regulations, the use of Halon 1301 is restricted to certain exceptional circumstances, with an anticipated decline in its usage, which may influence future assessments of '*ozone depletion impacts*', again raising issues regarding the VCMIs applicability in future contexts. Additionally, the use of potentially outdated datasets in ecoinvent means that the LCA data might not reflect current practices regarding the use of Halon 1301. Given this context, it is important to consider such limitations when utilizing LCA databases.

The stepwise inclusion of the remaining product classes in the system boundary weakens the correlation coefficient between the VCMI and '*ozone depletion impact*'. This diminished correlation is a result of including resource consumption in the VCMI calculation that is not directly associated with '*ozone depletion impact*', unlike crude oil consumption.

3.4.4 Energy resource: non renewable. Unlike the other environmental impacts discussed, '*energy resource: non-renewable*' is a resource-based impact that focuses on the depletion of non-renewable resources, such as coal, oil, and natural gas.[29] Since resource-based environmental impacts align with the input perspective of the VCMI, they can be directly influenced by resource consumption captured with the VCMI. In the case of '*energy use: non-renewable*', this means that higher fossil resource consumption leads to a higher environmental impact, independent of supply chain processes. Therefore, using resources that directly contribute to '*energy use: non-renewable*', such as fossil resources, could reliably approximate this environmental impact, even with technological changes in the supply chain.

However, it is important to note that when cradle-to-gate fossil resource consumption data is available, translating this data into the actual environmental impact '*energy resource: non-renewable*' requires minimal effort. This translation step involves multiplying the individual fossil resource consumption values by the existing corresponding characterization factors, resulting in the '*energy resource: non-renewable*' impact. Thus, when fossil resource consumption data is accessible, it is advisable to apply the relevant characterization factors to accurately quantify this environmental impact, as the impact considers more factors than just mass consumption, such as the energy density and rarity of resources.

4 Summary and conclusion

Various types of mass intensities are commonly used as "green chemistry metrics" with the intention to use them as indicators for environmental impacts. However, the literature still lacks a clear definition of system boundaries for the unambiguous calculation of mass intensities, and it is also unclear how well mass intensities really reflect environmental impacts. In this study we systematically analyze whether and with which system boundaries mass intensities can serve as a proxy to capture LCA environmental impacts. We used the Spearman correlation coefficient to assess the strength of the correlation between the mass intensities and sixteen LCA environmental impacts. We assumed that a high absolute Spearman correlation coefficient indicates a strong correlation so that using the corresponding mass intensity as indicator for environmental impacts appears sensible. On the contrary, a low absolute Spearman correlation coefficient suggests that the respective mass intensity is not meaningful for this purpose.

We studied mass intensities with eight different system boundaries, one defined by a gate-to-gate boundary (referring to it as "process mass intensity", PMI), and seven other mass intensities considering a cradle-to-gate system boundary, for which we introduced the new term Value Chain Mass Intensity (VCMI).

Our results show that the strengths of the correlations between the (gate-to-gate) PMI and all LCA environmental impacts are weak to very weak. In contrast, using the (cradle-to-gate) VCMI significantly improves the strengths of the correlations for fifteen out of sixteen LCA environmental impacts. This finding indicates that expanding system boundaries beyond the own factory gate is crucial in assessing sustainability and that considering value chain mass expenditures is essential for mass intensities to accurately reflect environmental performance. Due to data availability, our study focuses on chemicals with relatively simple value chains. However, we expect the impact of value chain mass expenditures on the meaningfulness of mass intensities to be even more pronounced for specialty chemicals, which typically have longer and more complex value chains.

Furthermore, we observe that mass intensities are ambiguously defined in current literature.[13,18,21,30,31] For instance, it is uncertain whether water inputs should be considered or excluded. Our results show a stronger correlation between mass intensities and most LCA environmental impacts, if water expenditures are excluded from the mass intensity calculations (see ESI†). This applies for example to '*climate change impact*', '*eutrophication*', and '*particulate matter formation*'; exceptions include '*energy resource use*', '*photochemical ozone formation*' and '*human toxicity*'. This means that a process mass intensity or value chain mass intensity excluding water is preferable compared to the variant with water considered if they are intended to be used as indicator for environmental impacts.

Moreover, not only is the inclusion of water ambiguously defined in current literature, but also whether inputs such as auxiliary materials for cleaning or natural gas for heat supply should be considered,[13,18,21,30,31] further demonstrating the lack of standardization in mass intensity metrics. Therefore, we analyzed the impact of seven specific product classes on the strength of the correlations between the VCMI and LCA environmental impacts. Our analysis reveals that the influence of product classes included in the system boundary on the strength of the correlation between the VCMI and LCA environmental impacts varies significantly. While the some system boundary expansions strengthen the correlation, further expansion to include other product classes even weakens it. This varying effect is attributable to the inclusion of key influencing resources, which vary across product classes. At the same time, we found that each environmental impact is associated with a different set of key resources that can serve as indicators for their respective environmental impacts. This variability highlights that a single metric with a fixed system boundary cannot adequately reflect the inherently multi-criteria nature of environmental sustainability.

In summary, our results lead us to the main conclusion that mass intensities should not be considered an appropriate proxy for a comprehensive environmental assessment. Since the (gate-to-gate) PMI shows only weak or very weak correlations with environmental impacts, expansion of the system boundary beyond the factory gate towards a VCMI would be required to obtain a more meaningful evaluation. Nevertheless, this comes with additional effort and challenges regarding data availability.

Additionally, even the VCMI, which considers the resources consumed along the entire value chain, carries risks when being used as a metric for environmental assessment. The meaningfulness of mass-based metrics depends significantly on the technologies used in the value chain, and these technologies may change over time. This dependency on the value chain renders mass-based metrics time-sensitive and potentially unreliable.

Furthermore, the dependency on the value chain also introduces another issue, which may even be more significant: comparing chemicals from different value chains, such as bio-based *versus* fossil-based chemicals, often results in a comparison of entirely different resources. For example, the mass intensity of a bio-based chemical will have a significantly higher contribution of biomass compared to a fossil-based chemical, which will have higher contributions of fossil resources. Comparing these two mass intensities ultimately results in a comparison of different resources, which will indicate distinct environmental impacts. For instance, a high mass intensity of a bio-based chemical might indicate higher '*eutrophication impact*' or '*land use*', whereas a high mass intensity of a fossil-based chemical could point to higher '*climate change impact*'. In light of the transition from a fossil-based chemical industry to a renewable one, relying on mass intensities alone to evaluate whether a new synthesis is advantageous could be misleading. Thus, instead of using mass intensities as proxy for environmental impacts, a simplified LCA that directly considers the environmental impacts of the resources used appears to be a more reasonable and reliable approach.

Especially given the current urgency of transitioning to a low-carbon economy, robust environmental impact assessments are paramount. As this transition is time-critical, it is crucial that decisions lead to the desired results. Relying on mass intensities as proxies for environmental impacts (such as '*climate change impact*') can mislead decision-makers and process developers, causing them to invest time and resources into processes that may ultimately prove counterproductive.

However, in complex value chains, such as those in the specialty or pharmaceutical industry, obtaining data to assess LCA environmental impacts poses significant challenges. A solution could be a database that offers aggregated data, such as LCA environmental impacts, specifically for these specialty chemicals. Additionally, to address data gaps, developing approaches to estimate LCA environmental impacts of specialty chemicals could simplify the data acquisition process. Various simplified LCA tools for non-LCA experts are available to reduce the burden of conducting an LCA during chemical development and to obtain early-stage LCA results. For example, the ESTIMATe[44] tool provides LCA results for the process development of CO_2-based chemicals, also considering technological development in the supply chain through decarbonization scenarios. Similar simplified LCA tools should be tailored to specific applications where environmental assessments are essential, but LCA data and expertise are currently lacking.

Finally, integrating life-cycle approaches in the chemical industry becomes more effective when there's a collective emphasis on life-cycle thinking. Collaborations between chemists, engineers and LCA experts as well as integrating life-cycle methodologies into chemistry curricula are complementary approaches to accelerate chemical industry's transformation.

Author contributions

Stefan Eichwald: conceptualization, methodology, software, validation, formal analysis, investigation, data curation, writing – original draft, visualization; Hesam Ostovari: methodology, writing – review & editing, supervision; Hannah Minten: methodology, validation, data curation, writing – review & editing, visualization; Janine Meyer-Waßewitz: conceptualization, methodology, validation, writing – review & editing, visualization; Dieter Förtsch: conceptualization, methodology, validation, writing – review & editing, visualization; Niklas von der Assen: conceptualization, methodology, writing – review & editing, supervision, funding acquisition.

Conflicts of interest

There are no conflicts to declare.

Data availability

The life-cycle inventory data used to calculate the environmental impacts and mass intensities of chemical processes are available through the commercially accessible ecoinvent database (**https://ecoinvent.org/**).

Additional data used for this study have been included as part of the ESI.†

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