Supplementary Information

Assessing Mass Intensity as a Green Chemistry Metric: Why Expanding System Boundaries is not Enough

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1. Ecoinvent datasets used for correlation analysis

In our study, we utilized the Ecoinvent database, which includes datasets for numerous chemical processes. To ensure consistency of selected data, we adhered to specific selection criteria. First, some chemical datasets in Ecoinvent approximate the material input using heuristic yields, since data availability is poor for many chemical processes. We consider the processes that use heuristics for the material inputs as insufficient for calculating the PMI and excluded them from this analysis. Second, the Ecoinvent database contains chemical datasets with location adjustments to reflect regional differences in raw material and electricity supply. To exclude these regional variations, we selected chemical processes exclusively located in Europe.

Third, certain processes produce multiple products (multifunctional processes). Ecoinvent allocates emissions and input materials to these products based on criteria such as produced mass or economic value. As the treatment of multifunctional processes is not fully clarified within the framework of Green Chemistry metrics, we excluded these multifunctional processes from our analysis. Fourth, for some processes, gate-to-gate data was not available. This lack of data made it impossible to conduct a gate-to-gate Process Mass Intensity (PMI) analysis for these processes. Consequently, these processes were also excluded from our study. By applying these criteria, we ensured that our analysis remained robust and focused on processes with comparable data, resulting in the investigation of 106 chemical processes (see Table S1).

Table S1: Ecoinvent datasets used for correlation analysis

Process name	Location	Reference product
1-propanol production	RER	1-propanol
2,4-dichlorotoluene production	RER	2,4-dichlorotoluene
2-methyl-2-butanol production	RER	2-methyl-2-butanol
4-methyl-2-pentanone production	RER	4-methyl-2-pentanone
acetaldehyde production	RER	acetaldehyde
acetic acid production, product in 98% solution state	RER	acetic acid, without water, in 98% solution state
acetic anhydride production, ketene route	RER	acetic anhydride
acetone production, from isopropanol	RER	acetone, liquid
acetylene production	RER	acetylene
acrylic acid production	RER	acrylic acid
adipic acid production	RER	adipic acid
alpha-naphthol production	RER	alpha-naphthol
ammonium carbonate production	RER	ammonium carbonate
ammonium nitrate production	RER	ammonium nitrate
ammonium nitrite production	RER	ammonium nitrite
ammonium sulfate production	RER	ammonium sulfate
aniline production	RER	aniline

Process name	Location	Reference product
ascorbic acid production	RER	ascorbic acid
azodicarbonamide production	RER	azodicarbonamide
benzyl alcohol production	RER	benzyl alcohol
bisphenol A production, powder	RER	bisphenol A, powder
bromopropane production	RER	bromopropane
butane-1,4-diol production	RER	butane-1,4-diol
butyl acetate production	RER	butyl acetate
butyl acrylate production	RER	butyl acrylate
carbon monoxide production	RER	carbon monoxide
chlorine dioxide production	RER	chlorine dioxide
chlorine production, liquid	RER	chlorine, liquid
chloroacetic acid production	RER	chloroacetic acid
chlorosulfonic acid production	RER	chlorosulfonic acid
chromium oxide production, flakes	RER	chromium oxide, flakes
cumene production	RER	cumene
cyclohexane production	RER	cyclohexane
cyclohexanol production	RER	cyclohexanol
cyclohexanone production	RER	cyclohexanone
decabromodiphenyl ether production	RER	decabromodiphenyl ether

dimethyl ether production	RER	dimethyl ether

Process name	Location	Reference product
dimethyl sulfate production	RER	dimethyl sulfate
dimethylaminopropylamine production	RER	dimethylaminopropylamine
dioxane production	RER	dioxane
DTPA production	RER	DTPA, diethylenetriaminepentaacetic acid
EDTA production	RER	EDTA, ethylenediaminetetraacetic acid
ethyl acetate production	RER	ethyl acetate
ethyl benzene production	RER	ethyl benzene
ethyl tert-butyl ether production, from bioethanol	RER	ethyl tert-butyl ether
ethylamine production	RER	ethylamine
ethylene bromide production	RER	ethylene bromide
ethylene dichloride production	RER	ethylene dichloride
ethylene oxide production	RER	ethylene oxide
ethylenediamine production	RER	ethylenediamine
fluorine production, liquid	RER	fluorine, liquid

formic acid production, methyl formate route	RER	formic acid
glycerine production, from epichlorohydrin	RER	glycerine

Process name	Location	Reference product
hydrazine production	RER	hydrazine
hydrochloric acid production, from the reaction of hydrogen with chlorine	RER	hydrochloric acid, without water, in 30% solution state
hydrogen fluoride production	RER	hydrogen fluoride
hydrogen peroxide production, product in 50% solution state	RER	hydrogen peroxide, without water, in 50% solution state
hydroquinone production	RER	hydroquinone
iodine production	RER	iodine
isobutyl acetate production	RER	isobutyl acetate
isopropyl acetate production	RER	isopropyl acetate
methyl ethyl ketone production	RER	methyl ethyl ketone
methyl formate production	RER	methyl formate
methyl tert-butyl ether production	RER	methyl tert-butyl ether
methylamine production	RER	methylamine

methylcyclohexane production	RER	methylcyclohexane
N,N-dimethylformamide production	RER	N,N-dimethylformamide
naphthalene sulfonic acid production	RER	naphthalene sulfonic acid
nitrous dioxide production	RER	nitrous dioxide
nitrous oxide production	RER	nitrous oxide
N-methyl-2-pyrrolidone production	RER	N-methyl-2-pyrrolidone

Process name	Location	Reference product
o-chlorotoluene production	RER	o-chlorotoluene
oxidation of manganese dioxide	RER	potassium permanganate
phosgene production, liquid	RER	phosgene, liquid
phosphorous chloride production	RER	phosphorous chloride
phthalic anhydride production	RER	phthalic anhydride
phthalimide production	RER	phthalimide
potassium nitrate production	RER	potassium nitrate
potassium sulfate production	RER	potassium sulfate
propanal production	RER	propanal
propionic acid production	RER	propionic acid
propyl amine production	RER	propyl amine
propylene glycol production, liquid	RER	propylene glycol, liquid
propylene oxide production, liquid	RER	propylene oxide, liquid

purified terephthalic acid production	RER	purified terephthalic acid
sodium amide production	RER	sodium amide
sodium chlorate production, powder	RER	sodium chlorate, powder
sodium cyanide production	RER	sodium cyanide
sodium dichromate production	RER	sodium dichromate
sodium dithionite production, anhydrous	RER	sodium dithionite, anhydrous
Process name	Location	Reference product
sodium hypochlorite production, product in 15% solution state	RER	sodium hypochlorite, without water, in 15% solution state
sodium oxide production	RER	sodium oxide
styrene production	RER	styrene
sulfur dioxide production, liquid	RER	sulfur dioxide, liquid
sulfur trioxide production	RER	sulfur trioxide
tert-butyl amine production	RER	tert-butyl amine
tetrahydrofuran production	RER	tetrahydrofuran
titanium dioxide production, chloride process	RER	titanium dioxide
titanium dioxide production, sulfate process	RER	titanium dioxide
toluene oxidation	RER	benzoic acid

trichloroethylene production	RER	trichloroethylene
trichloromethane production	RER	trichloromethane
triethyl amine production	RER	triethyl amine
trifluoroacetic acid production	RER	trifluoroacetic acid
vinyl acetate production	RER	vinyl acetate
vinyl chloride production	RER	vinyl chloride

2.

Spearman correlation between all environmental impacts and

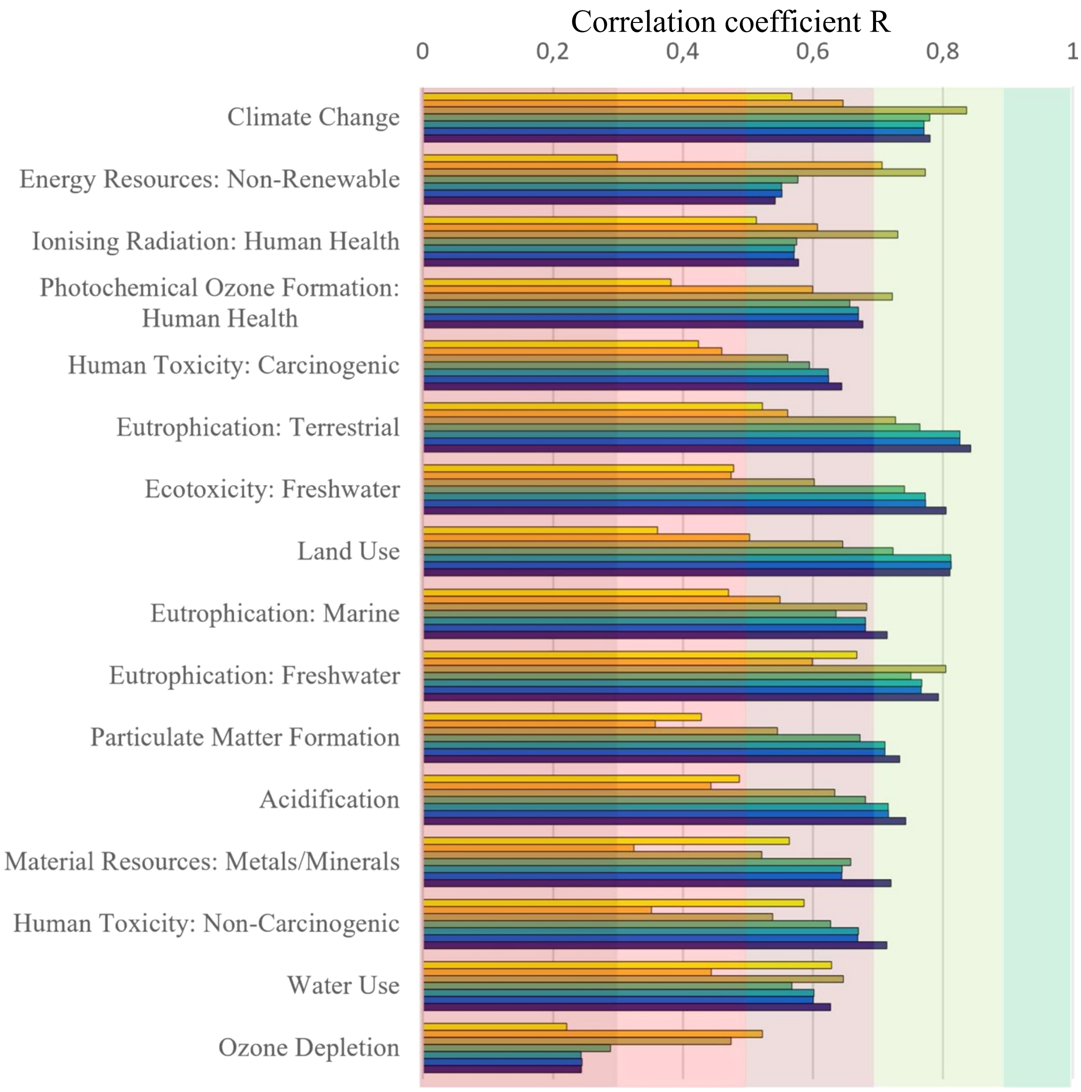
VCMI (excluding water)

VCMI_Chems_exw VCMI_Chems_Fossil_exw

VCMI_Chems_Fossil_Ene_exwVCMI_Chems_Fossil_Ene_MM_exw

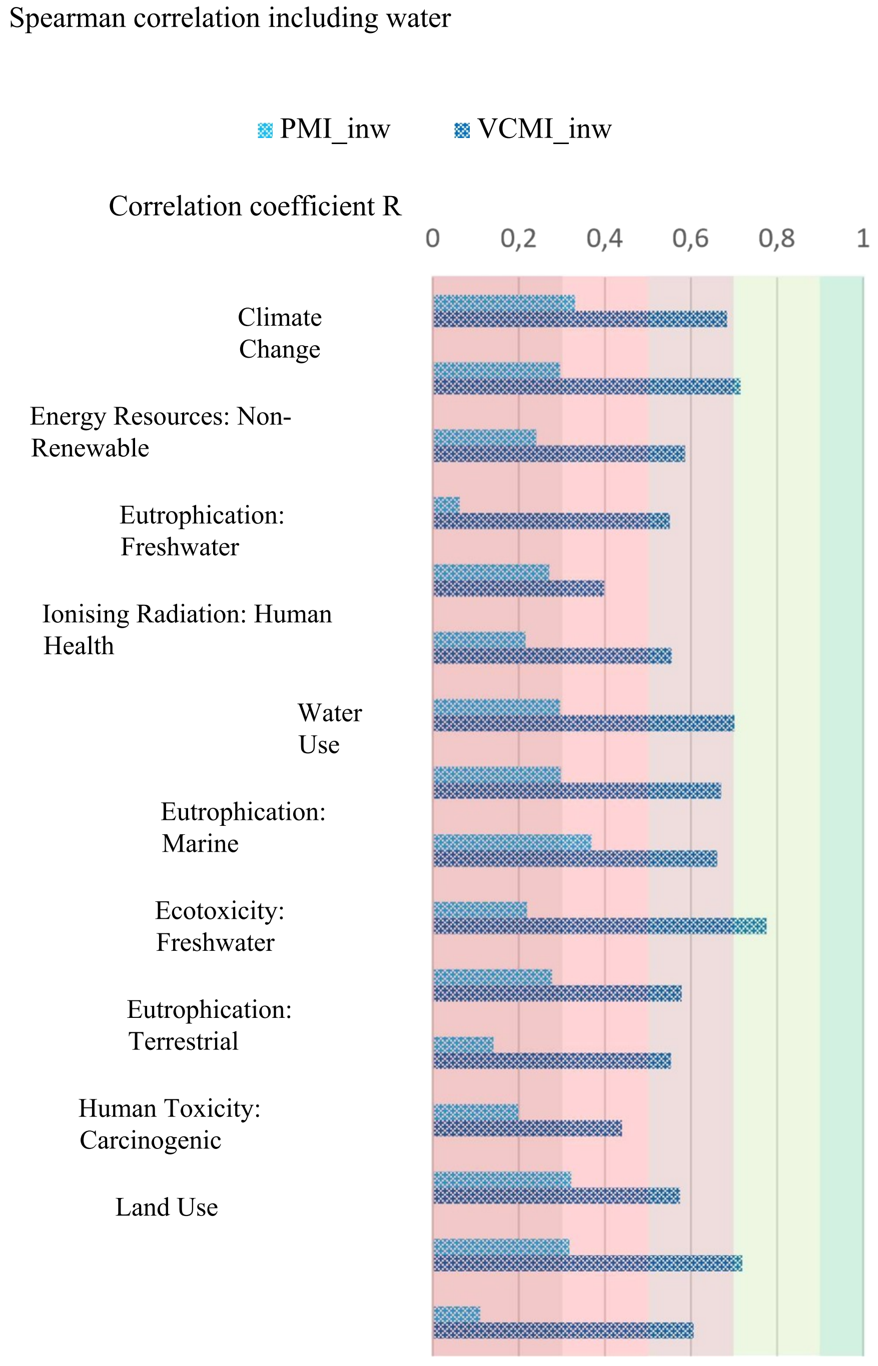
VCMI_Chems_Fossil_Ene_MM_Bio_exwVCMI_Chems_Fossil_Ene_MM_Bio_water_exw

VCMI_exw (All Product Categories)



3.

Figure S1: Values of Correlation coefficient R for the studied environmental impacts and all studied variations of VCMI excluding water (exw).



4.

Acidification

Human Toxicity: Non-Carcinogenic

Material Resources: Metals/Minerals

Particulate Matter Formation

Photochemical Ozone Formation: Human Health

Ozone Depletion

Figure S2: Values of Correlation coefficient R for the studied environmental impacts for the PMI and VCMI including water (inw)

5. Spearman correlation p-values

Table S2: Spearman correlation p-values for Process Mass Intensity including/excluding water (PMI inw/exw) and Value Chain Mass Intensity including/excluding water (VCMI inw/exw) for sixteen environmental impact categories

	PMI_inw	PMI_exw	VCMI_exw	VCMI_inw
Acidification	4.03E-03	1.26E-05	8.69E-11	8.33E-20
Climate Change	5.26E-04	9.55E-05	6.71E-16	6.30E-23
Ecotoxicity: Freshwater	2.08E-03	4.90E-06	5.83E-17	2.60E-25
Energy Resources: Non-Renewable	2.08E-03	9.65E-03	6.98E-18	2.04E-09
Eutrophication: Freshwater	1.29E-02	8.65E-05	3.95E-11	4.24E-24
Eutrophication: Marine	2.64E-02	8.80E-04	6.49E-10	8.45E-18
Eutrophication: Terrestrial	1.99E-03	1.08E-05	3.97E-15	1.02E-29
Human Toxicity: Carcinogenic	1.01E-04	2.92E-02	1.25E-14	9.22E-14
Human Toxicity: Non-Carcinogenic	1.49E-01	1.73E-05	7.70E-10	9.18E-18
Ionising Radiation: Human Health	5.25E-01	4.37E-03	9.58E-10	9.03E-11
Land Use	2.40E-02	1.31E-04	1.76E-22	6.54E-26
Material Resources: Metals/Minerals	4.09E-02	1.24E-07	2.45E-06	3.31E-18
Ozone Depletion	2.61E-01	1.91E-04	5.91E-12	1.20E-02
Particulate Matter Formation	7.70E-04	8.15E-05	1.22E-10	4.11E-19
Photochemical Ozone Formation: Human Health	9.13E-04	1.25E-03	4.18E-18	1.72E-15
Water Use	5.01E-03	5.43E-06	2.35E-05	6.38E-13

Table S3: Spearman correlation p-values for Value Chain Mass Intensity including/excluding water (VCMI inw/exw) for sixteen environmental impact categories

	VCMI Chems exw	**VCMI Chems_Fossil exw**	**VCMI Chems_Fossil Ene exw**	**VCMI Chems_Fos Ene_MM exw**	**VCMI Chems_Fos Ene_MM Bio exw**	**VCMI Chems_Fos Ene_MM Bio_water exw**
Acidification	1.24E-07	2.02E-06	3.18E-13	1.01E-15	6.59E-18	6.48E-18
Climate Change	2.24E-10	7.30E-14	6.63E-29	7.58E-23	4.39E-22	4.24E-22
Ecotoxicity: Freshwater	2.27E-07	2.88E-07	8.96E-12	1.15E-19	2.93E-22	2.81E-22
Energy Resources: Non-Renewable	1.88E-03	2.83E-17	3.01E-22	9.62E-11	8.96E-10	8.43E-10
Eutrophication: Freshwater	5.70E-15	1.19E-11	3.09E-25	1.95E-20	8.80E-22	1.02E-21
Eutrophication: Marine	3.79E-07	1.11E-09	7.50E-16	2.63E-13	9.78E-16	9.77E-16
Eutrophication: Terrestrial	9.47E-09	3.95E-10	1.17E-18	1.59E-21	1.19E-27	1.19E-27
Human Toxicity: Carcinogenic	6.15E-06	7.17E-07	3.98E-10	1.86E-11	9.41E-13	8.97E-13
Human Toxicity: Non-Carcinogenic	4.10E-11	2.24E-04	2.72E-09	6.59E-13	4.08E-15	4.59E-15
Ionising Radiation: Human Health	1.92E-08	5.47E-12	6.50E-19	1.18E-10	1.59E-10	1.68E-10
Land Use	1.47E-04	4.11E-08	8.11E-14	2.06E-18	4.29E-26	3.77E-26
Material Resources: Metals/Minerals	3.18E-10	6.98E-04	1.02E-08	1.76E-14	8.82E-14	9.46E-14
Ozone Depletion	2.32E-02	9.58E-09	2.91E-07	2.73E-03	1.21E-02	1.17E-02
Particulate Matter Formation	4.70E-06	1.73E-04	1.49E-09	2.98E-15	1.47E-17	1.43E-17
Photochemical Ozone Formation: Human Health	5.50E-05	1.15E-11	2.48E-18	2.14E-14	4.24E-15	4.13E-15
Water Use	5.40E-13	1.93E-06	6.87E-14	2.30E-10	9.24E-12	1.04E-11

5.

Pearson correlation coefficients

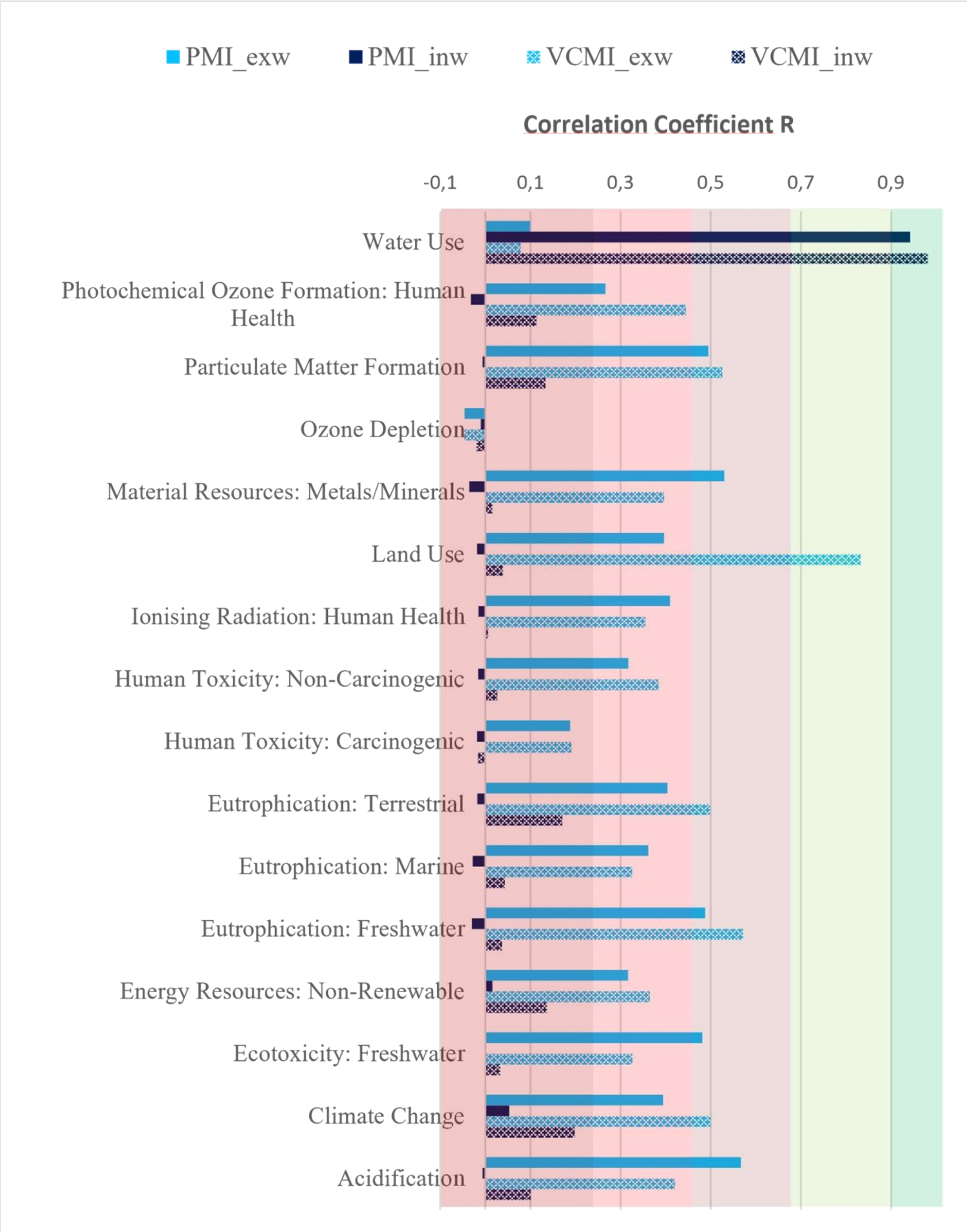


Figure S3: Values of Spearman correlation coefficient R for the studied environmental impacts.

Pearson p-Values

Table S4: Pearson p-values for Process Mass Intensity including/excluding water (PMI inw/exw) and Value Chain Mass Intensity including/excluding water (VCMI inw/exw) for sixteen environmental impacts

olol		**VCMI_inw**	**VCMI_exw**	**PMI_inw**	**PMI_exw**
Acidification	**Acidification**	1.00E-01	4.21E-01	0.948426323	2.39208E-10
Climate Change	**Climate Change**	1.98E-01	5.00E-01	0.589404134	2.85509E-05
Ecotoxicity: Freshwater	**Ecotoxicity: Freshwater**	3.30E-02	3.26E-01	0.987098849	1.76084E-07
Energy Resources: Non-Renewable	**Energy Resources: Non-Renewable**	1.36E-01	3.65E-01	0.874482358	0.00094615
Eutrophication: Freshwater	**Eutrophication: Freshwater**	3.68E-02	5.72E-01	0.759066318	1.16238E-07
Eutrophication: Marine	**Eutrophication: Marine**	4.34E-02	3.26E-01	0.77700805	0.000141644
Eutrophication: Terrestrial	**Eutrophication: Terrestrial**	1.71E-01	4.98E-01	0.854838601	1.74703E-05
Human Toxicity: Carcinogenic	**Human Toxicity: Carcinogenic**	-1.62E-02	1.91E-01	0.853299846	0.053238821
Human Toxicity: Non-Carcinogenic	**Human Toxicity: Non-Carcinogenic**	2.65E-02	3.85E-01	0.874228628	0.00091528
Ionising Radiation: Human Health	**Ionising Radiation: Human Health**	6.34E-03	3.55E-01	0.876687129	1.27294E-05
Land Use	**Land Use**	3.88E-02	8.32E-01	0.852446011	2.63962E-05
Material Resources: Metals/Minerals	**Material Resources: Metals/Minerals**	1.59E-02	3.96E-01	0.716051289	5.02397E-09
Ozone Depletion	**Ozone Depletion**	-1.95E-02	-4.67E-02	0.916854027	0.638638947
Particulate Matter Formation	**Particulate Matter Formation**	1.33E-01	5.25E-01	0.948912005	7.19815E-08
Photochemical Ozone Formation: Human Health	**Photochemical Ozone Formation: Human Health**	1.14E-01	4.45E-01	0.747733328	0.00572312
Water Use	**Water Use**	9.81E-01	7.88E-02	3.11848E-51	0.31185068

7.

Life Cycle Inventory Naphtha Steamcracking Process

The steamcracking process is crucial numerous chemical products.[1] Since the ecoinvent naphtha steamcracking process dataset is aggregated, we modeled the steamcracking process and replaced the ecoinvent steamcracking process with our modeled steamcracking process throughout the chemical supply chain. The process conditions of a steam cracker vary greatly from plant to plant. Therefore, the challenge is to choose the assumptions in such a way that the Life-Cycle Inventory allows general statements about the technology despite the many possible variants of steam-cracking. Our main source for the Life-Cycle Inventory is Ullmann's Encyclopedia of Industrial Chemistry.[2] We supplemented missing information with modeling assumptions based on a literature review. The following section presents our modeling assumptions. The full Life-Cycle Inventory is provided in a separate Excel data sheet.

Naphtha is distilled from natural resources and, thus, varies in its composition.[3] Due to different naphtha compositions, there are several options to characterize naphtha. We choose Full-Range Naphtha since it is the most common naphtha type used in Europe[2], which is the regional focus of the present study.

Steamcracking produces a mixture of numerous chemicals, with the composition depending on the steamcracking process. Target products of steamcracking are mainly olefins, such as ethylene and propylene.[4] However, numerous other hydrocarbons are produced as byproducts in the cracking process.[2] One factor affecting the product composition is the cracking severity, which reflects the extent to which the cracking reaction occurs.[2,4] The cracking severity is commonly expressed as the weight-based ratio of propylene to ethylene (P/E). Higher cracking severity results in higher ethylene yields.[2] Since the production volume of ethylene surpasses that of propylene[4], we assumed a highseverity steam cracking process (P/E = 0.45). Furthermore, the residence time of naphtha in the reactor greatly influences the composition of the products.[2] Typical residence times range from 0.1 to 0.5 seconds.[2] For our steamcracking Life-Cycle Inventory, we thus averaged the product composition for residence times between 0.1 and 0.5 seconds.

The amount of steam required for the steamcracking process is often expressed by the steam ratio. Typical values for naphtha steam-cracking steam ratios range from 0.4 to 0.5 kilogram steam per kilogram naphtha.[2] We conservatively assume of 0.5 kilogram steam per kilogram naphtha to rather overestimate than underestimate steam demand and the related environmental impact. We assume that the water for steam production is circulated, i.e., no fresh water is required for steam production during steamcracking operation. However, we consider the heat required to produce the steam. In typical steamcracking processes, the heat can be harnessed from product cooling to produce 50 - 80% of the energy required for steam generation.[2] We make the conservative assumption that 50% of heat for steam generation is supplied from product cooling off-heat. The remaining heat demand is provided by combustion of byproducts such as methane.

Furthermore, the steam-cracking process requires process water for cooling. On average, a steamcracking process requires 47000 m^3/h water. However, the process water is mainly circulated and only 5 – 10% must be renewed.[2] Again, we conservatively assume that 10% of process water must be renewed.

Regarding energy consumption, the steamcracking process requires heat and electricity. Electricity is mainly required for pumps, compressors, and cooling units. For the electricity demand, we assume 0.2778 kWh per kilogram of ethylene produced, which is a typical value for an average steamcracking plant.[2] The total heat demand is split into heat required for steam generation and specific heat demands for reaction, separation, and losses. We assume a specific energy demand of 23 MJ per kilogram ethylene, which is a typical value for an average steamcracking plant.[2] The total heat demand is satisfied by combustion of byproducts. We assume that excess heat will be exported. Therefore, we gave a credit for the heat that is exported.

A byproduct of steamcracking is pyrolysis gasoline, which is high in concentration of aromatic hydrocarbons (BTX) and other valuable chemicals. To separate and purify the individual chemicals, solvent extraction is a common process used in the industry.[5] To be consistent with the assumed high-severity cracking conditions, we choose the pyrolysis gasoline composition that results from high-severity steamcracking.[5] We took the energy demand and other utility demand per kilogram pyrolysis gas for the solvent extraction from Raoul et al..[6] Furthermore, we consider direct CO_2 emissions as well as CO_2 emissions resulting from waste water treatment, by closing the carbon balance between the solvent extraction input (pyrolysis gasoline) and the solvent extraction output (resulting product composition).

Since the steamcracker yield multiple products, the process is considered a multifunctional process. However, to calculate product-specific environmental impacts, we need to allocate the environmental impacts across all products. The DIN ISO Norm 14040 and 14044 provides a hierarchy of solutions to handle the multifunctionality of processes. The reader is referred elsewhere for further information.[7,8,9] The aggregated ecoinvent naphtha steamcracker is mass-based allocated. Therefore, to be consistent with the methodological choice of ecoinvent, we also used a mass-based allocation to allocate environmental impacts across all products of our modeled steamcracker.

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