



# Hourly marginal electricity mixes and their relevance for assessing the environmental performance of installations with variable load or power

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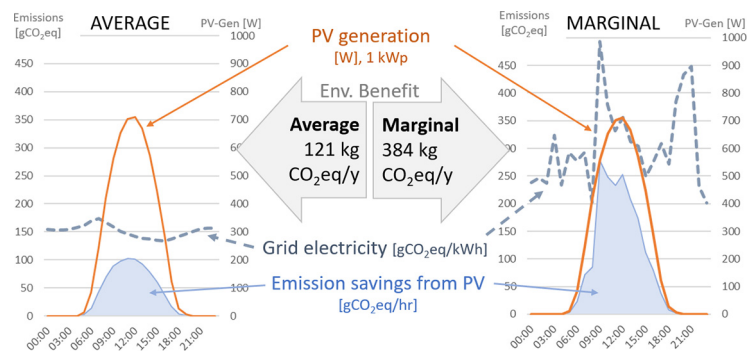
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## HIGHLIGHTS

- Up-to-date average and marginal generation mixes for the Spanish electricity grid
- Hourly and monthly emission factors determined based on life cycle assessment
- Marginal greenhouse gas emissions around 150 % higher than those of the average mix
- High relevance of hourly time resolution for assessing systems with variable load
- Higher variability in future electricity mix increases relevance of marginal impacts.

## GRAPHICAL ABSTRACT



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## ABSTRACT

The ongoing energy transition is causing rapid changes in the electricity system and, in consequence, the environmental impacts associated with electricity generation. In parallel, the daily variability of generation increases with higher shares of renewable energies. This affects the potential environmental impacts or benefits of devices with variable load or power, such as electric vehicles, storage systems or photovoltaic home systems. However, recent environmental assessments of the actual benefit of such systems are scarce, with existing assessments majorly using average grid mixes that are frequently outdated and disregard the dynamic nature of renewable generation. This article provides detailed hourly average and marginal electricity mixes for each month of the year, determined for Spain as an illustrative country with a diversified (renewable) power generation portfolio that experienced a rapid change in the last years. These are combined with specific life-cycle emission factors for each generation technology. Main drivers for the impacts of the marginal mix turn out to be natural gas plants and imports, but also pumped hydropower due to its comparably low storage efficiency. Applied to a hypothetical photovoltaic rooftop installation, the differences between environmental assessments on hourly and on annual basis are found to be surprisingly low when assuming that the generated electricity replaces the average grid mix, but substantial when considering the marginal generation mix (i.e., the generation technologies that respond to a change in demand at a given time). This highlights the importance of considering the dynamics of the electricity system and the corresponding marginal electricity mixes when optimizing flexible load or generation technologies under environmental aspects.

## 1. Introduction

The transition away from fossil fuels towards renewables is advancing with rapid pace, fuelled by the continuously decreasing prices of renewable generation technologies, increasingly ambitious national and international

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emission reduction targets and not at least the will to decrease energy dependency, an aspect that has gained substantial importance only very recently (IEA, 2020; IRENA, 2022; Harvey, 2022). These fast changes pose challenges not only for grid operators and regulators on operational side, but also for system analysts that aim at quantifying the potential environmental impacts of goods, services or products and that need to deal with a rapidly changing energy landscape. Considering that electricity is an important contributor to environmental impacts in many product categories, the use of up-to-date electricity mixes is essential for meaningful environmental assessments (Carvalho and Delgado, 2017; Helmers and Weiss, 2017; Olindo et al., 2021). In this light, the electricity mixes provided by the well-known ecoinvent or GaBi inventory databases are deemed outdated despite regular updates (Moreno Ruiz et al., 2021; Olindo et al., 2021; sphera, 2021), adding uncertainty to the assessments relying on them. In addition, also the time resolution used for the assessment plays an important role when evaluating the benefits of installations with non-constant output such as solar home systems (Beloïn-Saint-Pierre et al., 2020; Jordaan et al., 2021). Here, significant discrepancies can be observed between studies using high-resolution load and generation curves for determining their economic benefit and those based on average values (Ayala-Gilardón et al., 2018; Cao and Sirén, 2014; Weniger et al., 2014). The same applies to the environmental assessment of electricity generation or consumption with non-constant load profiles in general (Elzein et al., 2019; Kopsakangas-Savolainen et al., 2017). The emission intensity of the grid electricity varies along the day, and correspondingly do the associated environmental impacts. In fact, a new tariff scheme with hourly discrimination has recently been introduced in Spain (MITECO, 2021), mainly to adjust the electricity prices to the changing generation profile, but at the same time incentivizing a more conscious consumption of electricity and the shift of flexible loads to hours of low demand ('valley hours'). Previous studies in other countries found noteworthy discrepancies between assessments using annual average grid mixes and a higher (hourly) time resolution (Olindo et al., 2021). Using hourly emission intensity, significant potential for emission reductions by smart load management have been identified for Finland (Kopsakangas-Savolainen et al., 2017), France (Milovanoff et al., 2018) and Germany (Kono et al., 2017; Jochem et al., 2015), in case of the latter by adjusting the charge profile of electric vehicles to the hours of lowest emission intensity of the grid. Another recent work found dynamic modelling of electricity on hourly basis for Hungary to influence the life-cycle impact results significantly (Kiss et al., 2020; Rupp et al., 2019), while Vuarnoz and Jusselme (2018) provided hourly emission profiles for the Swiss grid, though without any specific case study. For Spain, attempts have been made to update the (comparably old) inventory data contained in the latest version of ecoinvent, but with a focus on modelling a more up-to-date electricity mix and without accounting for seasonal or hourly fluctuations (Puig-Samper Naranjo et al., 2021), or based on simulations without providing the corresponding emission factors (Victoria and Gallego-Castillo, 2019). Despite these attempts, studies that consider the hourly and seasonal variability of the electricity generation for environmental assessments are generally scarce (Jordaan et al., 2021).

Also, there is an ongoing discussion about the use of marginal emission factors for environmental assessments. Unlike the average grid mix, the marginal electricity mix considers the response of the generation park to a change in demand i.e., determines which technologies would be used for covering an additional demand at a certain point of time (Weidema et al., 1999). These can be short-term marginal or long-term marginal, depending on scope and time horizon. Short-term marginal mix refers to the generation mix that responds to a change in demand from one moment to the other within a given generation park, while long-term marginal mix describes the structural change of the generation park over time, i.e., the generation technology that would be installed additionally (or decommissioned) for satisfying increasing (or decreasing) demand (Consequential LCA, 2020; Vandepaer et al., 2019).

Long-term marginal mixes have been developed for the ecoinvent database for most European countries, with a time horizon until 2030 (Moreno Ruiz et al., 2021; Vandepaer et al., 2019). For Spain, energy systems

modelling has been applied for determining the development of the electricity sector until 2050, but describing the general evolution of the generation mix without focusing on the marginal changes (García-Gusano et al., 2017; Iribarren et al., 2020). Short-term marginal mixes have been developed for Germany based on energy systems modelling with the aim of optimizing electric vehicle (EV) charging behaviour (Jochem et al., 2015), and based on merit-order simulation, though without accounting for pumped hydropower or imports, which can be important marginal sources (Regett et al., 2018). Marginal mixes have been developed and applied to EV charging for the years 2012–2014 for France, Germany, Great Britain, Belgium, Spain and Italy, finding noteworthy differences between average annual and hourly emission factors, but also between hourly average grid mixes and hourly marginal mixes (Milovanoff et al., 2018). For Portugal, Garcia and Freire (2016) determined marginal emission factors by a linear-regression approach, though assuming that only coal and gas satisfy additional demands, while Carvalho et al. (2020) used a general algebraic modelling system (GAMS) for estimating the hourly marginal generation technology and the corresponding impacts of EV charging strategies. Average marginal mixes for all EU countries were reported by Corradi (2018) based on the data provided by Electromaps (2020), though only on an annual basis without considering hourly fluctuations. One of the most recent and comprehensive works on marginal electricity mixes is the one by Arvesen et al. (2021), who provided hourly average and marginal electricity mixes and emission factors for the European grid based on energy systems modelling for the year 2050. For Spain, Arcos-Vargas et al. (2020) used marginal electricity generation for assessing the environmental performance of PV systems, but assuming natural gas combined cycle (NGCC) plants to exclusively cover the additional electricity demand.

All previously mentioned works found significant discrepancies between assessments using annual average electricity mixes, hourly average and hourly marginal emission intensities when assessing or optimizing variable loads. However, even though there is increasing evidence that the time resolution plays a major role for a realistic and meaningful assessment, no recent estimation of the hourly average and marginal electricity mix and its corresponding environmental impacts is available. This is particularly relevant due to the recent change in the legislative framework and corresponding quickly accelerating uptake of renewables, leading to a quickly changing generation landscape.

In order to overcome the previously described gaps, this paper determines short-term marginal emission factors for Spain, considering hourly and seasonal fluctuation and providing average and marginal electricity mixes with an hourly resolution for each month of the year, based on most recent data available (2021). The high temporal resolution also allows to evaluate the appropriateness of the new three-period tariff scheme for incentivizing electricity consumption during periods of low emission intensity. As a case study, the obtained marginal emission factors are then applied for quantifying the environmental performance of photovoltaic (PV) solar rooftop installations under consideration of the marginal hourly electricity mix replaced by the additional generation. However, the obtained marginal emission factors are not limited to PV assessments, but relevant to all environmental assessments of the Spanish electricity system requiring hourly time resolution, including also analyses on EV deployment and energy storage systems. Moreover, the choice of Spain as a country with a diversified (renewable) power generation portfolio enriches the overarching discussion on the relevance of marginal electricity mixes when it comes to assessing the environmental performance of installations with variable load or power, a research topic of general scientific and international relevance.

## 2. Methodology

### 2.1. Data sources

Data on historical electricity generation are taken from the Spanish grid operator (REE), which provides time series of the electricity generation mix, corresponding CO<sub>2</sub> emissions and spot market price since 2014 with

hourly resolution (REE, 2021). Though these time series provided by REE also include CO<sub>2</sub> emissions, these are direct emissions and therefore do not include upstream processes. For obtaining a more meaningful evaluation of the potential environmental impacts, we use indicators for each of the different generation technologies based on life cycle assessment (LCA) as detailed in Section 2.2. Generation data for the PV installation used for the case-study are taken from a previous assessment (Wuebben and Peters, 2022), assuming an average rooftop installation in central Spain (Madrid). For imported electricity (from France and Portugal, we rely on data available on the entso-e platform, where hourly generation data is available for most European countries, though at higher level of aggregation. The corresponding time series and the obtained hourly electricity mixes are provided in the online supplementary information (SI).

## 2.2. Environmental impacts of electricity generation technologies

Regarding the life-cycle environmental impacts of the power generation technologies relevant to the Spanish electricity mix, this study considers the same technology portfolio addressed in García-Gusano et al. (2017) and Navas-Anguaita et al. (2018) but with updated inventory data. For this purpose, the impacts of each generation technology contributing to the electricity mix are calculated based on ecoinvent 3.8 (Moreno Ruiz et al., 2021). The results for all considered technologies and all EF3.0 impact categories are available in the supplementary information. Regarding the life cycle impact assessment method, the Environmental Footprint 3.0 method—whose use is supported by the European Commission (Sala et al., 2018)—is applied to evaluate the following indicators: climate change, acidification, use of fossil resources, and use of mineral and metal resources. These indicators are typically addressed when assessing energy systems (Valente et al., 2020) since they effectively capture key environmental concerns regarding both renewable and non-renewable energy technologies. For instance, non-renewable energy technologies are usually associated with concerns on greenhouse gas emissions (captured by the climate change indicator) and abiotic resource depletion of fuels (captured by the indicator “use of fossil resources”), which are often correlated (Valente et al., 2019). On the other hand, renewable power generation technologies are often associated with different concerns on abiotic resource depletion due to the required extraction of elements (captured by the indicator “use of mineral and metal resources”). Other indicators such as acidification are typically relevant to both non-renewable (e.g., coal-based) and renewable (e.g., cultivated biomass-based) energy systems. In any case, the supplementary data files provided for this work allow for a quick determination of the impacts for all other available categories.

For pumped hydro and import, no inventory or environmental impact data are provided by the previously mentioned studies, disregarding imports and corresponding impacts. In addition, the impacts of pumped hydro are assumed to be equal to those of other hydropower. However, performing pumped hydro an energy storage function rather than just generating power, it requires special consideration, taking into account the electricity consumed during storage (i.e., in pumping mode). The impacts of pumped hydro are therefore calculated based on the corresponding inventory datasets taken from ecoinvent (Moreno Ruiz et al., 2021), but adjusted to the annual pumping electricity mix updated to 2021 according to Section 2.3. The full set of life cycle impacts used for each of the generation technologies are provided in the supplementary information files.

## 2.3. Determining the hourly average and marginal electricity mix

### 2.3.1. Hourly average electricity mix

For determining the hourly average electricity mix for each month, we rely on historical time series as described in Section 2.1. Due to the rapid change in generation structure, especially the sharp drop of coal in 2019, and the potential impact of the COVID pandemic on the electricity grid in 2020 we only use data from 2021. The phase out of coal generation has already been implemented in recent energy systems models and is in line with the objectives of the Spanish Energy and Climate plan (García-

Gusano et al., 2018; PNIEC, 2020). For each generation technology and in each hour of the year, the life-cycle environmental impacts in terms of climate change, acidification, use of fossil resources, and use of mineral and metal resources are calculated per kWh generated by multiplying the average share of each generation technology within each hour of the month with its specific impacts (available in the supplementary files provided with this article). The hourly generation mixes are then averaged over each month of the year for every hour of the day, obtaining an average daily profile for each month of the year. For imported electricity, the hourly mix is determined in the same way, allowing to accurately determine also the fluctuations in the impact intensity of imported electricity with the same time resolution.

As a case-study, the environmental benefits of a residential PV rooftop installation are then assessed using the hourly generation mixes determined for each month. For this purpose, the electricity generated by the PV-SC system in each hour is multiplied by the impacts of the avoided electricity, obtaining a benefit for the avoided electricity. Subtracting the impacts associated with the PV installation itself then gives the potential environmental benefits of the PV installation (Section 2.5).

### 2.3.2. Hourly marginal electricity mix

Second, instead of calculating average generation mixes, we determine the relative change of the share of each generation technology due to an increase/decrease in demand (i.e., the marginal electricity mix) (Böing and Regett, 2019; Regett et al., 2018). For this purpose, we take the intermittent renewable generation (wind and solar) and the total electricity demand as exogenous, and assume that an increase/decrease in demand would be covered by a corresponding increase/decrease of controllable generation technologies, i.e., NGCC, coal, nuclear, hydro and other thermal power plants, besides imports (Corradi, 2018). The marginal change of imports/exports is assumed to be endogenous when following the same trend as the total demand; for instance, imports increase when demand increases, meaning that imports can be considered to serve as an additional generation technology and effectively satisfy demand. If imports/exports show a different trend (e.g., imports increase though domestic demand decreases), this is considered to be due to exogenous causes (mainly price differences), and the corresponding amount is then added to/ subtracted from the total demand. Similarly, generation technologies that show an opposite trend to the demand (e.g., increased generation while demand decreases) are not considered for the marginal mix since the driver in this case is not the change in demand.

The change in the controllable mix from the previous ( $h-1$ ) to the current ( $h$ ) hour is then the marginal generation mix (Corradi, 2018; Kleinert et al., 2018), which involves a share ( $margin_{tec,h}$ ) of each controllable power generation technology ( $tec$ ). Correspondingly,  $margin_{tec,h}$  is expressed as a fraction (or percentage) that the given generation technology contributes to the total generation within the considered hour (Eq. (1)).

$$margin_{tec,h} = (Gen_{tec,h} - Gen_{tec,h-1}) / (\sum_{tec} Gen_{tec,h} - \sum_{tec} Gen_{tec,h-1}) \quad (1)$$

where  $Gen_{tec,h}$  stands for the electricity generated (MWh) by technology  $tec$  in hour  $h$ .

Unfortunately, there is no information about curtailments available in the time series, even on request to the grid operator. However, this is a relevant aspect, since for hours of renewable curtailment, an increase in demand could be covered by simply reducing the amount of curtailed electricity and have no further impacts. We determine hours where curtailment is necessary in days where all of the following conditions are met (i) the share of sun and wind, nuclear and cogeneration and waste exceeds 90 % of the total generation share (nuclear, waste and cogeneration have a very limited margin of reacting to changes in demand), (ii) the exported net flow is positive (electricity is exported, indicating an excess of electricity in the domestic market) and the total amount of electricity exported is above 98 % of the maximum export capacity, (iii) the pumped hydro plants operate in pumping mode, and (iv) the electricity price is below the five-year average minus the standard deviation. For hours where electricity generation

is curtailed, the marginal environmental impacts are considered to be zero. Being these assumptions based on own judgement, we tested the impact of variations in the set thresholds and find even variations  $\pm 30\%$  to have negligible impact on the results. The strongest constraint is the relation between exported electricity and export capacity, but even this can be varied between 90 % and 100 % with no major changes in the marginal mix. The supplementary data files provided with this article allow for testing the influence of these parameters on the results.

As previously, the mean value of the hourly generation shares is then calculated for each month, thus obtaining an average daily profile for each month of the year; for imports, the annual average marginal mix is used. This, again, is used for assessing the performance of the hypothetical PV installation under consideration of the marginal electricity mix.

### 2.3.3. Average marginal electricity mix consumed by pumped hydro

For pumped hydro, the main share of impacts is originated in the electricity consumed during storage. According to the used ecoinvent dataset, 1.4 kWh of electricity are consumed for providing 1 kWh of electricity provided by pumped hydro. Correspondingly, the electricity mix assumed for pumped hydro plays an important role, especially regarding marginal electricity (where pumped hydro contributes a much higher share than in the average grid mix). The detailed hourly time series allow for determining the hours when pumped hydro plants are in pumping (storage) mode and therefore the corresponding marginal electricity mix used for charging this type of storage. However, an hourly time resolution does not make sense in this case, since the electricity stored in one hour cannot be assigned to another hour when the pumped hydro plant discharges (generates). Therefore, the marginal electricity of pumped hydro is determined as the annual average marginal mix of all the hours where pumped hydro is in storage mode (i.e., it does not generate, but consumes). The marginal mix

consumed by pumped hydro and the corresponding inventory data are provided in the SI.

### 2.3.4. Electricity imports

Cross-border exchanges of electricity play an important role for balancing the grid and reduce the demand for dedicated storage capacity. Being imports a relevant contributor to the overall electricity mix (both average and marginal), also the hourly variability of the impact intensity of imported electricity needs to be considered. For this purpose, hourly time series obtained from the entso-e platform are used and the impact intensity of both the French and the Portuguese electricity mix is determined for each hour, following the previously described approaches for both the average and the marginal electricity mixes. This allows to consider the specific impact intensity of imports which, unlike the other generation technologies varies following daily and seasonal (annual) patterns. For Morocco, the third country that is connected with the Spanish peninsula, no hourly time series are available. For the imports from Morocco, the average impact intensity obtained from the ecoinvent database is therefore used.

### 2.4. Future generation mix

The ongoing transition of the electricity system will lead to continuously increasing shares of renewables and correspondingly decreasing GHG intensity of the electricity mix. However, when using the current electricity mix for the assessment of technologies or energy systems, this effect is disregarded, thus potentially overestimating potential environmental benefits or impacts. Therefore, the consideration of future developments of the electricity mix, though uncertain, can help to provide a more realistic picture of the potential environmental impacts of the assessed system over its lifetime (García-Gusano et al., 2017). In addition, the increasing fluctuation of the electricity mix caused by the higher shares of renewables will

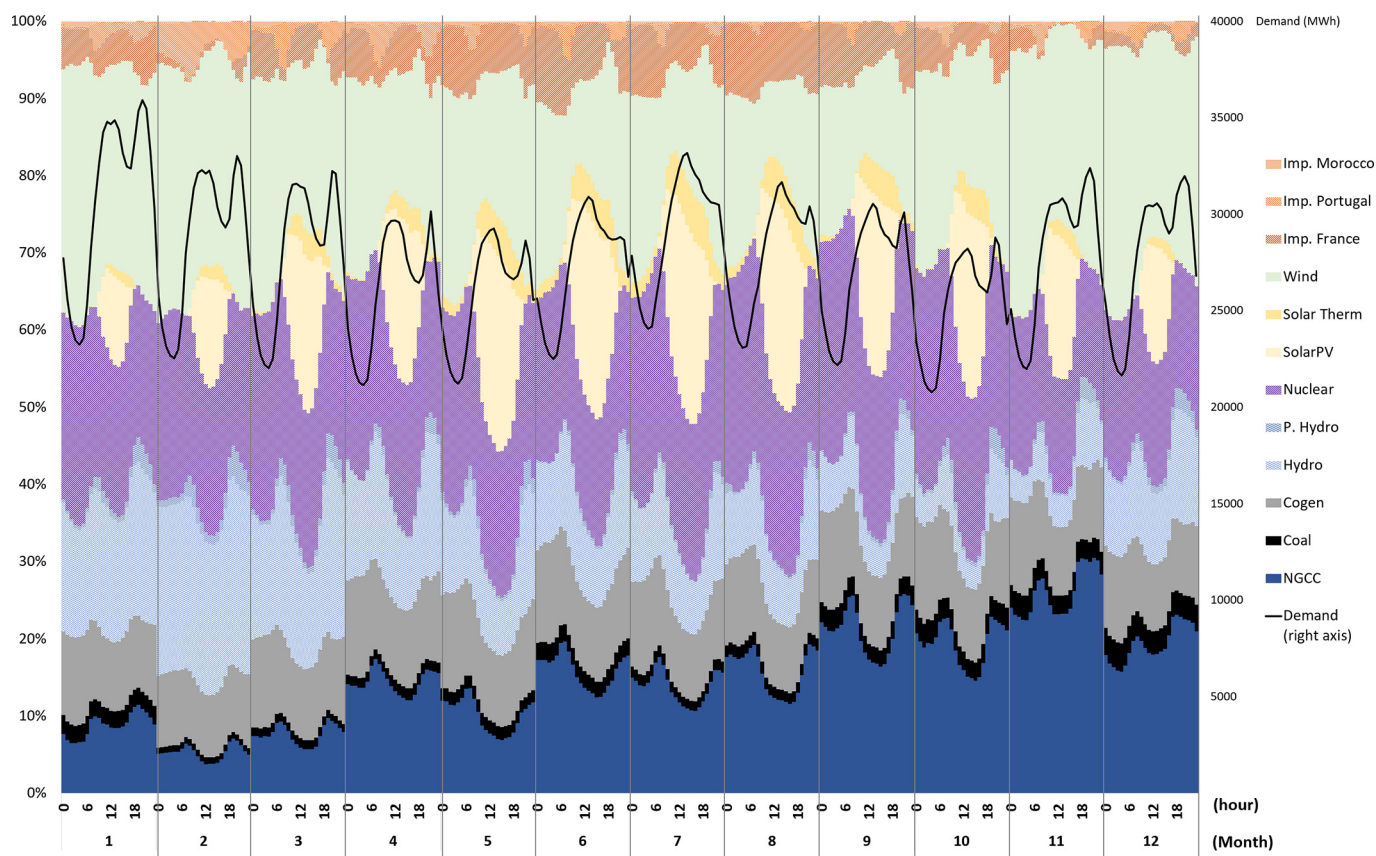


Fig. 1. Hourly average generation mix by month in 2021.

lead to a higher importance of assessments considering the seasonal and daily variations, especially for systems with varying load such as PV or electric vehicles (Arvesen et al., 2021; Kiss et al., 2020). While a detailed modelling of the future electricity mix with hourly time resolution is out of scope of the present work, we attempt to provide an idea of the possible implications for the average and marginal hourly mix in future. This is done by decomposing the historical time series into two seasonal (monthly and hourly) components, plus the long-term trend. Then, taking average annual values obtained from long-term energy system models with yearly time resolution (García-Gusano et al., 2018; Navas-Anguita et al., 2018), the identified cyclic components can be superposed to the annual average share of each generation technology, obtaining a hypothetical future generation profile with hourly resolution for each month. While insufficient for a detailed assessment of the future generation mix, it allows to provide a picture of the relevance of time resolution for assessing future electricity generation and the corresponding limitations of energy system models with yearly time resolution. Details about the approach are provided in the SI.

2.5. Implementation in ecoinvent

In order to provide a readily applicable dataset for further use in LCA, the obtained annual average and marginal electricity mixes are combined with the existing ecoinvent database, updating the generation mixes to the most recent values while using the same generation technologies as in the original datasets. Due to the higher precision of the ecoinvent datasets (broader set of generation technologies) these are grouped into clusters, assuming that the distribution within each cluster does not change when modifying its contribution to the overall mix (e.g., the shares between lignite and hard coal within the coal generation remain constant when changing the total contribution of coal to the electricity mix). The corresponding

inventory tables and the inventory datasets for import into LCA software (ILCD and JSONLD format) are provided as supplementary files (see SI).

2.6. Environmental performance of the PV system

For determining the relevance of time resolution and corresponding hourly electricity mixes for the environmental performance of energy systems with varying load, we assess a hypothetical PV installation in central Spain. By using the marginal electricity mix as determined in Section 2.3.2., the consequence of injecting a certain amount of additional electricity into the grid (or of avoiding its generation in case of self-consumption) are evaluated. For this purpose, the PV electricity generated within each hour ( $Gen_{PV,h}$ ) is multiplied by the impacts associated with the (avoided) generation of the corresponding (average or marginal) electricity mix determined for the corresponding hour and month, and the impacts attributed to the production of that PV electricity are subtracted ( $impact_{PV}$ ). For each environmental life-cycle indicator under consideration ( $impact$ ), this can be expressed according to Eq. (2) as:

$$Benefit_{PV,h} = Gen_{PV,h} * \sum_{tec} (marg_{tec,h} * impact_{tec,h}) - impact_{PV} \quad (2)$$

The PV system consists of a hypothetical 1 kW<sub>p</sub> PV installation in central Spain (Madrid). Hourly generation data are estimated for a monocrystalline PV system with optimum angle and azimuth based on historical irradiation data from the European Union's Photovoltaic Geographic Information System from 2011 to 2016, averaged over each month (Wuebben and Peters, 2022). The total annual PV generation is 1619 kWh per installed kW<sub>p</sub> of generation capacity, and the assumed lifetime of the system is 20 years.

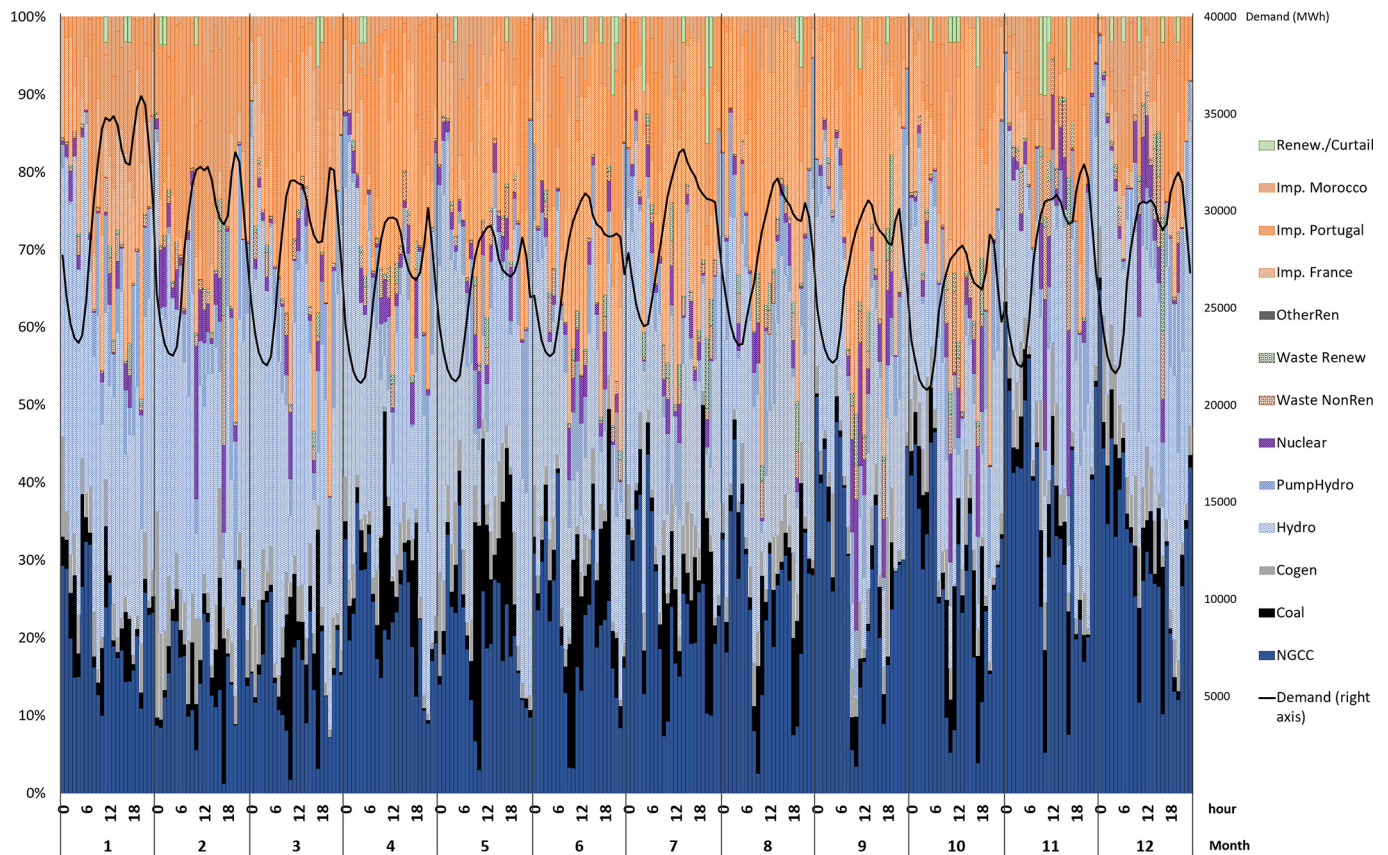


Fig. 2. Hourly marginal generation mix by month in 2021.

For the PV system, the environmental impacts associated with its production and installation ('impact<sub>PV</sub>') are obtained from the ecoinvent database (dataset: 'market for photovoltaic slanted-roof installation, 3 kW<sub>p</sub>, single-Si, panel, mounted, on roof') and amount for the considered impact categories to (values per kWp):

- Climate change (GWP): 129.4 kg CO<sub>2</sub> eq/kW<sub>p</sub>
- Acidification (AP): 0.75 mol H<sup>+</sup> eq/kW<sub>p</sub>
- Use of fossil resources (FR): 1.60 GJ<sub>prim</sub>/kW<sub>p</sub>
- Use of mineral and metal resources (MMR): 0.0124 kg Sb eq/kW<sub>p</sub>

### 3. Results

#### 3.1. Average mix

The average hourly generation mix for each month is displayed in Fig. 1. A clear correlation between the availability of hydropower resources and the share of fossil generation (mainly NGCC) can be observed, highlighting the importance of these technologies for grid stability due to their flexibility. In addition, the higher contribution of solar energy leads to a stronger daily fluctuation during these months. While a total demand above the annual average can also be observed for the months of July and August, this is the case also in winter (November–February), and therefore does not explain the different generation shares. The highest shares of renewables are observed in the spring months, with both stronger wind and availability of hydropower resources. A similar profile is obtained when using not only the time series for 2021, but the whole available timespan from 2015 to 2021, though the share of coal generated electricity then increases on

the expense of NGCC. The corresponding figure for the time series 2015–2021 is provided in the SI.

#### 3.2. Marginal mix

Fig. 2 shows the average hourly marginal electricity mixes determined for each month of the year 2021. As previously, the corresponding results for the timespan 2015–2021 are provided in the SI for comparison. Unlike the average generation mix, the marginal mix hardly contains any solar and wind energy (since these are not controllable technologies, they do not follow the load except in situations of curtailment), and also only very small nuclear and cogeneration components. The latter provide a baseload and usually do not follow the demand variations, and changes in demand therefore hardly affect these technologies. On the other hand, hydropower and pumped hydropower gain relevance, being these the technologies mostly used for short-term balancing of load and generation, along with electricity imports. In particular, the interconnections with France and Portugal seem to play a major role for balancing the Spanish electricity grid and are therefore highly relevant also to the decarbonisation of the national electricity system. Natural gas and coal show similar shares and similar daily profiles as determined for the average mix, though with higher variability. High shares of fossil generation are mainly obtained in early morning hours and during afternoon peaks.

#### 3.3. Environmental impacts of the average mix

The hourly carbon footprint of the Spanish electricity mix when applying a life-cycle approach according to Section 2.2 is displayed in Figs. 3 and 4.

TIER 1	Hourly emissions [gCO <sub>2</sub> eq/kWh] - average mix												
	hour	Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep	Oct	Nov	Dec
	00:00	134.4	95.7	120.0	152.9	151.4	177.0	154.1	164.6	201.5	202.9	213.8	192.8
	01:00	132.9	96.5	123.2	153.2	151.9	179.6	153.8	167.3	200.9	200.9	212.7	191.2
	02:00	132.8	97.4	124.5	155.1	151.7	183.6	153.6	167.2	200.7	199.1	213.5	191.3
	03:00	132.2	98.8	125.6	155.9	152.0	184.0	154.6	167.3	201.8	202.9	212.0	191.1
	04:00	132.9	99.7	126.2	156.8	154.0	186.2	157.9	170.0	204.1	204.2	212.8	191.0
	05:00	133.9	99.3	128.7	158.6	156.0	188.2	161.8	172.9	206.9	206.6	217.0	193.0
	06:00	136.0	99.4	131.0	167.3	161.6	194.1	169.1	175.0	212.1	211.9	223.1	194.6
	07:00	140.2	101.4	129.2	169.7	161.1	193.1	173.3	177.6	215.6	208.1	223.9	194.9
	08:00	138.5	101.8	125.6	166.6	154.4	185.6	166.5	171.1	215.8	207.2	222.6	194.6
	09:00	135.7	99.9	122.4	161.7	146.9	178.0	158.5	160.8	204.8	199.5	215.4	190.0
	10:00	132.9	96.7	117.9	158.4	138.1	170.6	150.7	151.2	188.4	187.1	206.8	185.7
	11:00	131.7	93.8	116.0	155.0	134.8	167.2	146.3	146.5	180.3	177.6	201.4	183.0
	12:00	130.0	91.8	114.7	152.4	132.1	163.6	142.5	144.3	175.4	173.5	200.9	181.6
	13:00	129.6	91.9	112.5	149.7	130.0	161.1	139.0	142.3	172.9	168.4	200.7	181.8
	14:00	130.2	92.0	112.4	149.5	127.4	158.5	137.2	141.2	172.5	167.5	201.1	184.1
	15:00	132.3	93.9	112.9	149.1	126.4	156.1	135.3	139.9	171.5	167.3	204.8	186.7
	16:00	135.6	95.9	115.5	149.5	126.7	156.5	134.4	138.3	173.7	171.3	215.2	195.5
	17:00	141.6	101.1	121.3	152.7	126.7	160.1	137.2	139.2	180.1	180.1	232.0	205.9
	18:00	143.3	106.1	126.3	158.1	128.9	165.0	141.4	143.6	189.2	198.3	231.8	204.2
	19:00	143.2	107.2	127.5	160.0	135.8	166.9	146.0	153.9	203.4	206.1	230.5	202.0
	20:00	140.2	105.2	122.9	158.9	142.1	171.5	151.4	163.7	209.1	200.1	228.3	199.7
	21:00	138.5	101.6	121.2	156.8	142.9	172.5	156.1	168.5	209.3	199.0	231.3	199.7
	22:00	138.1	99.8	121.0	158.7	146.8	175.4	156.6	168.4	211.5	200.5	233.0	201.4
	23:00	136.3	97.8	121.4	159.7	149.5	179.1	156.7	167.5	209.4	200.4	229.2	199.2
	Avg	135.6	98.4	121.3	156.8	141.6	172.6	150.3	157.1	194.9	192.1	217.0	193.0

Fig. 3. Hourly average carbon footprint of electricity per month in 2021: colour coding for whole year (red = above annual average, green = below annual average). Dark grey shaded hours mark peak hours (highest electricity prices), light grey the intermediate hours (intermediate price level), and white the valley hours (lowest electricity prices).

Both figures show the same values but with a different colour coding in order to visualize the seasonal and hourly variability. Fig. 3 relates to the annual average, showing values that are below the annual average in green, and those above in red, thus visualizing seasonal fluctuations over the year. Fig. 4 colour-codes each month individually and therefore highlights the hourly fluctuation of the electricity carbon intensity for each month individually (see SI for tabulated values and remaining impact categories). The daily average varies between 98.4 (February) and 217.0 g CO<sub>2</sub> eq/kWh (November), between 35 and 60 % above the values provided by the Spanish grid operator (REE, 2021) (which vary between 61.2 in February and 160.6 g CO<sub>2</sub>eq/kWh in November; see SI for tabulated values). A clear seasonal component is observed, with the highest values in July and the autumn months, and the lowest ones in spring, when wind and hydro resources are most abundant. Interestingly, the new tariff scheme does not seem to correspond with the emission intensity: the defined peak hours with highest prices, aimed at disincentivizing the consumption of electricity during these hours, do not match with the hours of highest emission intensity, especially during morning hours and in summer (Fig. 4).

### 3.4. Environmental impacts of the marginal mix

When looking at the marginal carbon footprints, the picture is less homogeneous. Highest impacts are again found during late autumn months, but also in early summer (May–July) and lowest again in early springtime (Fig. 5, same colour coding scheme as for Fig. 3). However, the daily profile is significantly less smooth. High values are obtained in the morning and midday hours, when demand is ramping up and during the afternoon peak hour, while low values accumulate along the late evening, with a clearly

visible time shift towards later hours in summer; see Fig. 6. Interestingly, the seasonal variability is much less pronounced than for the average electricity mix, with very similar patterns obtained in Figs. 5 and 6 (+/- 7 % variation of the monthly average along the year for the marginal carbon footprint vs. ± 34 % for the average). Also, the coincidence between hours of peak electricity prices and GHG emissions is higher and seems to fit roughly, although a seasonal differentiation in the tariff scheme could improve this. The corresponding tables and heat maps for the remaining environmental indicators (acidification, use of fossil resources, and use of mineral and metal resources) are provided in the SI.

### 3.5. Environmental benefits of PV

As seen in the previous section, the environmental performance of the electricity varies significantly over the day, but also the different month of the year. For energy systems with variable demand or generation profiles such as PV installations, storage systems or electric vehicle charging, disregarding this variability will add significant error the corresponding assessments. Fig. 7 shows the match between electricity carbon footprint, PV generation and the corresponding environmental benefits of the hypothetical 1 kW<sub>p</sub> residential PV system as defined in Section 2.6 when using the hourly average and the hourly marginal emission factors. Due to the different technologies involved in the average and marginal electricity production mixes (Sections 3.1 and 3.2), a remarkable difference is found in the GHG emission savings estimated under each approach, as visualised by the different size of the shaded area in Fig. 7.

Table 1 summarises the average impacts obtained for the electricity mix determined via the different approaches over the whole year, and the

TIER 1	Hourly emissions [gCO <sub>2</sub> eq/kWh] - average mix											
hour	Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep	Oct	Nov	Dec
00:00	134.4	95.7	120.0	152.9	151.4	177.0	154.1	164.6	201.5	202.9	213.8	192.8
01:00	132.9	96.5	123.2	153.2	151.9	179.6	153.8	167.3	200.9	200.9	212.7	191.2
02:00	132.8	97.4	124.5	155.1	151.7	183.6	153.6	167.2	200.7	199.1	213.5	191.3
03:00	132.2	98.8	125.6	155.9	152.0	184.0	154.6	167.3	201.8	202.9	212.0	191.1
04:00	132.9	99.7	126.2	156.8	154.0	186.2	157.9	170.0	204.1	204.2	212.8	191.0
05:00	133.9	99.3	128.7	158.6	156.0	188.2	161.8	172.9	206.9	206.6	217.0	193.0
06:00	136.0	99.4	131.0	167.3	161.6	194.1	169.1	175.0	212.1	211.9	223.1	194.6
07:00	140.2	101.4	129.2	169.7	161.1	193.1	173.3	177.6	215.6	208.1	223.9	194.9
08:00	138.5	101.8	125.6	166.6	154.4	185.6	166.5	171.1	215.8	207.2	222.6	194.6
09:00	135.7	99.9	122.4	161.7	146.9	178.0	158.5	160.8	204.8	199.5	215.4	190.0
10:00	132.9	96.7	117.9	158.4	138.1	170.6	150.7	151.2	188.4	187.1	206.8	185.7
11:00	131.7	93.8	116.0	155.0	134.8	167.2	146.3	146.5	180.3	177.6	201.4	183.0
12:00	130.0	91.8	114.7	152.4	132.1	163.6	142.5	144.3	175.4	173.5	200.9	181.6
13:00	129.6	91.9	112.5	149.7	130.0	161.1	139.0	142.3	172.9	168.4	200.7	181.8
14:00	130.2	92.0	112.4	149.5	127.4	158.5	137.2	141.2	172.5	167.5	201.1	184.1
15:00	132.3	93.9	112.9	149.1	126.4	156.1	135.3	139.9	171.5	167.3	204.8	186.7
16:00	135.6	95.9	115.5	149.5	126.7	156.5	134.4	138.3	173.7	171.3	215.2	195.5
17:00	141.6	101.1	121.3	152.7	126.7	160.1	137.2	139.2	180.1	180.1	232.0	205.9
18:00	143.3	106.1	126.3	158.1	128.9	165.0	141.4	143.6	189.2	198.3	231.8	204.2
19:00	143.2	107.2	127.5	160.0	135.8	166.9	146.0	153.9	203.4	206.1	230.5	202.0
20:00	140.2	105.2	122.9	158.9	142.1	171.5	151.4	163.7	209.1	200.1	228.3	199.7
21:00	138.5	101.6	121.2	156.8	142.9	172.5	156.1	168.5	209.3	199.0	231.3	199.7
22:00	138.1	99.8	121.0	158.7	146.8	175.4	156.6	168.4	211.5	200.5	233.0	201.4
23:00	136.3	97.8	121.4	159.7	149.5	179.1	156.7	167.5	209.4	200.4	229.2	199.2
Avg	135.6	98.4	121.3	156.8	141.6	172.6	150.3	157.1	194.9	192.1	217.0	193.0

Fig. 4. Hourly average carbon footprint of electricity per month in 2021: colour coding for each month individually (red = above monthly average, green = below monthly average). Dark grey shaded hours mark peak hours (highest electricity prices), light grey the intermediate hours (intermediate price level), and white the valley hours (lowest electricity prices).

TIER 2	Hourly marginal emissions [gCO <sub>2</sub> eq/kWh]											
	hour	Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep	Oct	Nov
00:00	291.2	247.3	171.3	259.1	221.3	267.2	238.0	239.3	324.8	326.7	325.1	351.3
01:00	245.2	189.8	195.7	193.5	224.6	240.2	246.5	249.2	294.0	380.6	325.6	341.5
02:00	226.4	237.7	166.1	210.4	230.1	259.2	237.7	262.4	260.4	339.0	295.4	333.0
03:00	297.3	251.7	254.4	250.0	240.6	265.0	324.0	273.5	231.9	364.1	335.0	377.7
04:00	285.8	197.3	265.1	256.9	361.7	282.3	233.7	247.0	249.9	397.4	422.6	422.5
05:00	331.2	248.9	257.9	300.8	324.1	306.6	292.4	270.6	333.8	409.8	384.2	418.3
06:00	247.4	230.1	173.7	308.0	294.3	286.4	277.2	243.8	263.5	310.4	336.0	352.2
07:00	278.3	293.9	212.4	278.9	281.0	264.3	292.1	242.6	297.9	268.9	353.1	297.3
08:00	245.9	259.5	258.9	272.8	258.8	184.5	202.7	215.4	314.3	282.3	300.1	264.0
09:00	181.6	257.6	295.2	319.7	535.3	379.7	493.6	277.1	230.5	347.3	332.3	280.5
10:00	389.3	295.2	409.8	479.7	515.1	464.6	379.4	400.6	286.4	391.7	367.7	397.7
11:00	362.0	318.3	303.6	434.2	425.0	513.5	332.1	308.9	277.8	430.9	375.9	252.0
12:00	234.7	272.5	230.1	321.7	465.6	402.3	356.2	277.4	292.8	386.6	345.8	274.4
13:00	273.8	280.1	215.1	242.9	302.6	311.2	312.7	338.5	273.2	350.0	361.9	323.0
14:00	180.6	199.0	201.3	268.8	254.4	282.4	304.5	242.2	266.2	317.8	249.9	236.7
15:00	213.7	222.9	255.0	233.3	280.5	305.7	249.2	236.4	264.9	299.1	267.0	305.4
16:00	326.1	375.8	263.0	290.7	416.2	263.0	276.8	269.5	240.5	388.1	337.2	485.3
17:00	258.7	389.3	508.6	391.5	400.3	391.7	309.0	220.5	219.2	390.0	288.0	258.6
18:00	221.0	200.8	206.6	487.6	472.6	376.5	271.8	319.7	277.9	405.5	237.1	220.1
19:00	244.4	231.4	185.9	208.2	270.1	467.9	385.0	326.0	289.2	242.2	278.3	206.0
20:00	234.3	208.6	180.0	185.8	199.7	358.1	432.9	558.4	212.0	232.1	270.3	218.5
21:00	263.8	274.5	244.4	249.8	187.6	318.9	448.3	261.0	249.8	242.0	236.8	275.5
22:00	210.8	255.3	193.5	206.3	216.4	244.1	231.0	224.5	225.9	243.4	256.0	247.5
23:00	230.9	210.3	160.7	196.4	162.0	163.3	200.9	208.0	252.1	233.9	298.1	267.0
Avg	261.4	256.2	242.0	285.3	314.2	316.6	305.3	279.7	267.9	332.5	315.8	308.6

Fig. 5. Hourly marginal carbon footprints of electricity per month in 2021: colour coding for whole year. Dark grey shaded hours mark peak hours (highest electricity prices), light grey the intermediate hours (intermediate price level), and white the valley hours (lowest electricity prices).

corresponding benefits obtained from the installation of the PV system. Compared to the average grid mix, the marginal electricity mix shows 80 % higher GHG emissions but similar acidification impacts and lower resource demand (17 % lower for FR and 68 % for MMR). The latter is a direct result of its high share of hydropower and imports (with an important share coming from France, where nuclear dominates), while renewables, typically major drivers of mineral and metal resource demand, do not contribute substantially to the marginal mix except in (still rare) cases of curtailment. The recent average mix is also substantially different from that of the ecoinvent database, with significantly lower GHG emissions and acidification impact, but higher mineral and metal resource use, indicating the progress of the energy transition and the importance of using up-to-date electricity mixes for environmental assessments.

Interestingly, when applied to the PV system and estimating the corresponding environmental benefits, the differences between using the hourly and the annual average electricity mix are comparably small under GHG emissions aspects, with a discrepancy of around 8 %. Acidification benefits are around 10 % lower when considering the time-variability of the PV generation, and fossil resource use 7 % below. Only under aspects of mineral and metal resource use, the hourly assessment gives about 60 % higher benefits. Except for this impact category, using the annual average grid mix therefore tends to overestimate the actual benefits of the PV installation.

However, when considering the marginal mix, this trend is reversed, and the benefits obtained from the PV installation under an hourly approach are estimated between 12 and 25 % higher than when using the annual marginal mix (except for acidification, where they are 10 % lower). While this indicates a good fit of the PV generation with the hours of higher environmental impacts associated with the marginal generation, the second

peak in the marginal emissions occurs typically close to sunset and cannot be covered by PV systems.

#### 4. Discussion

The finding that the GHG emissions of the marginal generation mix are significantly higher than the average grid mix are in general alignment with those of previous studies, where the majority finds the marginal mix to be associated with higher GHG emissions than the average grid mix (Arcos-Vargas et al., 2018; Garcia and Freire, 2016; Jochem et al., 2015; Ma et al., 2012; Pareschi et al., 2017). However, the reasons for this vary widely; while some studies are based on the simple assumption that additional demand would always be covered by fossil power plants, we identify pumped hydropower and imports to be major drivers of impacts, an aspect hardly addressed by previous works. Especially pumped hydro covers an important share of the variable generation (the marginal generation) while at the same time showing a high electricity demand during storage (1.4 kWh/kWh), thus becoming a major factor for the total marginal impacts. Imports, being another major instrument for stabilising the grid and reacting to short-term changes in demand, are a second hotspot for the marginal impacts. Therefore, also the hourly average and marginal emissions intensity of the major electricity importers (France and Portugal in the case of Spain) need to be considered for a meaningful assessment. Compared to our initial approach using annual average and marginal mixes taken from literature, the consideration of the temporal variability of the emission intensity of imports decreases both the average and the marginal mix significantly, indicating that cross-border exchange is effective for balancing neighbouring grids and reducing overall emission intensity



TIER 2	Hourly marginal emissions [gCO <sub>2</sub> eq/kWh]											
hour	Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep	Oct	Nov	Dec
00:00	291.2	247.3	171.3	259.1	221.3	267.2	238.0	239.3	324.8	326.7	325.1	351.3
01:00	245.2	189.8	195.7	193.5	224.6	240.2	246.5	249.2	294.0	380.6	325.6	341.5
02:00	226.4	237.7	166.1	210.4	230.1	259.2	237.7	262.4	260.4	339.0	295.4	333.0
03:00	297.3	251.7	254.4	250.0	240.6	265.0	324.0	273.5	231.9	364.1	335.0	377.7
04:00	285.8	197.3	265.1	256.9	361.7	282.3	233.7	247.0	249.9	397.4	422.6	422.5
05:00	331.2	248.9	257.9	300.8	324.1	306.6	292.4	270.6	333.8	409.8	384.2	418.3
06:00	247.4	230.1	173.7	308.0	294.3	286.4	277.2	243.8	263.5	310.4	336.0	352.2
07:00	278.3	293.9	212.4	278.9	281.0	264.3	292.1	242.6	297.9	268.9	353.1	297.3
08:00	245.9	259.5	258.9	272.8	258.8	184.5	202.7	215.4	314.3	282.3	300.1	264.0
09:00	181.6	257.6	295.2	319.7	535.3	379.7	493.6	277.1	230.5	347.3	332.3	280.5
10:00	389.3	295.2	409.8	479.7	515.1	464.6	379.4	400.6	286.4	391.7	367.7	397.7
11:00	362.0	318.3	303.6	434.2	425.0	513.5	332.1	308.9	277.8	430.9	375.9	252.0
12:00	234.7	272.5	230.1	321.7	465.6	402.3	356.2	277.4	292.8	386.6	345.8	274.4
13:00	273.8	280.1	215.1	242.9	302.6	311.2	312.7	338.5	273.2	350.0	361.9	323.0
14:00	180.6	199.0	201.3	268.8	254.4	282.4	304.5	242.2	266.2	317.8	249.9	236.7
15:00	213.7	222.9	255.0	233.3	280.5	305.7	249.2	236.4	264.9	299.1	267.0	305.4
16:00	326.1	375.8	263.0	290.7	416.2	263.0	276.8	269.5	240.5	388.1	337.2	485.3
17:00	258.7	389.3	508.6	391.5	400.3	391.7	309.0	220.5	219.2	390.0	288.0	258.6
18:00	221.0	200.8	206.6	487.6	472.6	376.5	271.8	319.7	277.9	405.5	237.1	220.1
19:00	244.4	231.4	185.9	208.2	270.1	467.9	385.0	326.0	289.2	242.2	278.3	206.0
20:00	234.3	208.6	180.0	185.8	199.7	358.1	432.9	558.4	212.0	232.1	270.3	218.5
21:00	263.8	274.5	244.4	249.8	187.6	318.9	448.3	261.0	249.8	242.0	236.8	275.5
22:00	210.8	255.3	193.5	206.3	216.4	244.1	231.0	224.5	225.9	243.4	256.0	247.5
23:00	230.9	210.3	160.7	196.4	162.0	163.3	200.9	208.0	252.1	233.9	298.1	267.0
Avg	261.4	256.2	242.0	285.3	314.2	316.6	305.3	279.7	267.9	332.5	315.8	308.6

Fig. 6. Hourly marginal carbon footprints of electricity per month in 2021: colour coding for each month individually (red = above monthly average, green = below monthly average). Dark grey shaded hours mark peak hours (highest electricity prices), light grey the intermediate hours (intermediate price level), and white the valley hours (lowest electricity prices).

(Milovanoff et al., 2018). Only for Morocco detailed time series for the electricity grid are unavailable, and still annual average values are used (though the amount of electricity imported from Morocco is very small and with limited impact on the total environmental profile of the Spanish electricity mix).

Future developments are expected to lead to increasing shares of renewables and a correspondingly higher variability of the marginal electricity. For instance, Arvesen et al. (2021) found future marginal mixes for Europe to show lower carbon intensity than the average mix, combined with a shift towards lower daytime marginal emissions due to the increasing share of renewables. While we find renewables to contribute yet only a minor share to the marginal mix, this will likely change in future. To provide an idea of the consequences of these changes, we combine a simple time series decomposition with forecasts of future generation shares from a national energy systems model with yearly time resolution. The results (graphs provided in Section 6 of the SI) show that the strong daily and seasonal cycles of solar and wind pose serious challenges to the electricity grid but will also lead to an increasing share of renewables in the marginal mix, especially during daytime and in summer seasons. This might lead to a significant reduction in the marginal emission intensity, but also to a higher sensitivity to the hour and month when the electricity is consumed. Being a detailed modelling of future marginal mixes out of the scope of the present work, the corresponding forecast exercise is provided only as supplementary information and used for a merely qualitative outlook.

In any case, the consideration of storage systems for balancing the fluctuations and the corresponding marginal impacts during charge operation will be of increasing relevance. In fact, pumped hydropower, currently still the only relevant storage technology, is one of the main drivers for

the marginal emissions. A more detailed forecast of the hourly and monthly average and marginal generation mixes, and corresponding emission factors might thus help to increase the reliability of assessments of energy storage systems and to optimise their operation under environmental aspects. In a first attempt, the marginal and average mix for pumped hydro storage provided in this work (electricity mix used when pumped hydro is in storage mode) can be a good proxy for more accurately estimating the potential impacts of stationary energy storage systems.

For the 1 kW<sub>p</sub> PV installation used as case study, the average annual GHG emission savings are estimated at 131 kgCO<sub>2</sub>eq/kW<sub>p</sub>y when using the annual average grid mix (2021), 121 when using the average mix with hourly time resolution and 384 kgCO<sub>2</sub>eq/kW<sub>p</sub>y using the hourly marginal grid mix. This is situated in the lower range of the values obtained from installer quotes in a previous work, which were situated between 191 and 1430 kgCO<sub>2</sub> eq/kW<sub>p</sub>y (Wuebben and Peters, 2022). These values, obtained by comparing quotes from commercial PV installers for a representative building revealed a very high variability and lack of common basis for estimating GHG emissions savings. They therefore highlight the need for a comprehensive assessment framework for achieving comparability.

When comparing the impacts of the annual average and marginal mix as presented in Table 1 with the values obtained when implementing the same mixes in the ecoinvent database structure according to Section 2.5, some discrepancies can be observed. The results obtained when directly calculating the impacts of the generation mix are between 5 and 15 % lower than when implementing the same mix into the ecoinvent database structure. This is a result of the consumption-based calculation in ecoinvent, accounting for transformation losses and therefore additional generation that is not considered when using the generation values from the grid operator as

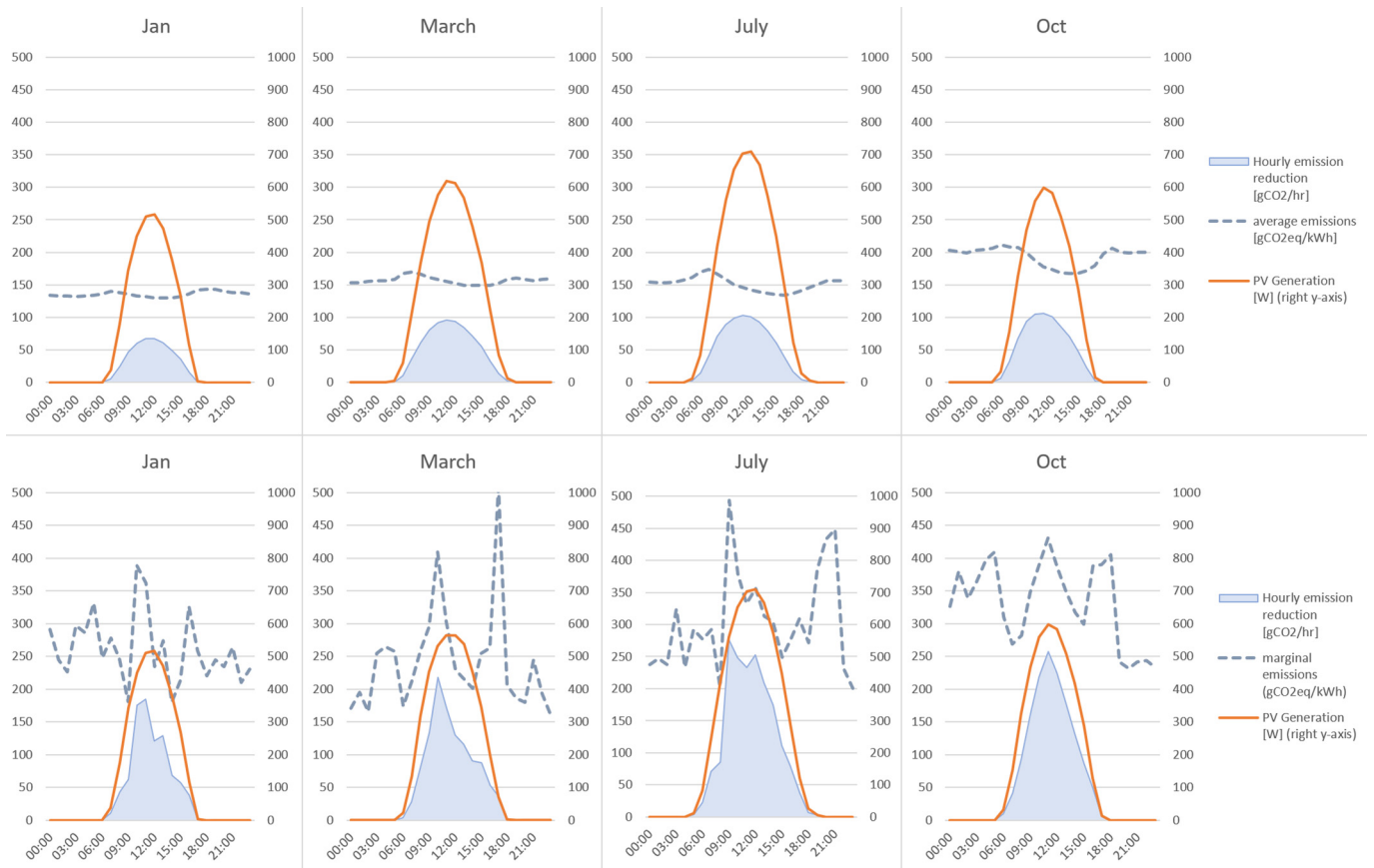


Fig. 7. PV generation and carbon footprint of the average (upper row) and marginal (lower row) Spanish electricity mix, and corresponding direct GHG emission savings due to PV in winter, spring, summer and autumn.

described in Section 2.2. The implementation of dynamic hourly electricity mixes within LCA software coupled with the ecoinvent database would therefore constitute a promising future work.

5. Conclusions

We estimate and provide the most recent (2021) hourly average and hourly marginal Spanish electricity generation mixes for each month of the year and apply these to a hypothetical residential photovoltaic (PV) installation in central Spain. Combining the electricity mixes with the life-cycle environmental profiles of the different electricity generation

technologies allows for a more detailed assessment of the actual environmental impacts associated with non-constant generation or consuming technologies such as PV or electric vehicle charging, as well as of energy storage technologies. The carbon intensity of the grid electricity varies between 98 and 217 g CO<sub>2</sub> eq/kWh when considering the average generation mix, and between 225 and 309 g CO<sub>2</sub> eq/kWh for the marginal generation mix.

In consequence, the price discrimination recently introduced by the Spanish government (mandatory peak and valley tariff scheme) supports consumer participation in reducing the impacts associated with electricity generation by considering hourly variations. While the peak and valley times do not coincide with the carbon intensity of the hourly average

Table 1

Comparison of the annual average environmental impacts of electricity generation and the corresponding benefits of a hypothetical 1 kW<sub>p</sub> PV installation according to different approaches (REE hourly: direct emissions according to data provided by the grid operator; ecoinvent annual: impacts of the annual average generation mix [“Market for electricity, low voltage ES”] according to version 3.8 of the ecoinvent database; Annual average: impacts of the annual average generation mix; Hourly average: impacts of the hourly average generation mix, integrated over the year; Annual marginal: impacts of the annual marginal generation mix; Hourly marginal: impacts of the hourly marginal generation mix, integrated over the year).

Topic	Indicator	REE	ecoinvent	Average mix		Marginal mix		Unit
Electricity generation (per kWh)	GWP	110.5	392.5	161.1		290.7		g CO <sub>2</sub> eq/kWh
	AP	-	3.33	0.49		0.49		mmol H <sup>+</sup> eq/kWh
	FR	-	8.50	5.29		4.45		MJ <sub>prim</sub> /kWh
	MMR	-	0.37	0.757		0.24		g Sb eq/kWh
Benefits of PV (per kW <sub>p</sub> and year)	GWP	34.9	505.8	Annual	131.4	Annual	341.0	kg CO <sub>2</sub> eq/kWh
				Hourly	120.7	Hourly	383.9	
				100 %		100 %		113 %
				100 %		100 %		90 %
	AP	-	4.64		0.04		0.04	mol H <sup>+</sup> eq/kWh
					0.04		0.04	
	FR	-	12.16		6.96		5.60	GJ <sub>prim</sub> /kWh
					6.48		6.29	
				100 %	93 %		100 %	112 %
	MMR	-	0.590		1.213		0.375	kg Sb eq/kW <sub>p</sub>
				1.927		0.470		
			100 %	159 %		100 %	125 %	

generation mix (and could therefore seem to be counterproductive), they do fairly fit the hourly marginal impacts. However, due to the strong seasonal component in the electricity mix (mainly due to the seasonal differences in hydropower and wind availability), a more differentiated price discrimination could further increase benefits for consumers willing to participate in such a scheme.

Interestingly, for the PV system the high time resolution does not change the results substantially when assuming that the electricity generated by the PV installation replaces the average grid mix. The actual benefit of the PV system when considering an average hourly time resolution is between 7 and 10 % less than when simply applying the annual average grid mix (i.e., using average grid mix tends to overestimate PV benefits). Only for mineral and metal resource use the outcome is different, with the actual benefit being around 60 % higher than when using annual average values. However, when considering that an additionally generated kWh of electricity does not substitute the average grid mix, but the marginal mix (i.e., the mix of generation technologies that responds to a change in demand at the given hour and month), the picture changes. In this case, the estimated GHG emission savings from the PV-SC system are around 160 % higher than for the annual average grid mix, while fossil resource savings are 26 % lower and mineral and metal resource savings 57 % higher. This can be attributed to the relatively high share of hydropower and imports within the marginal mix in Spain, in turn of comparably low GHG emission intensity (especially for the imports from France). Also, the consideration of the hourly and seasonal variations is more important for the marginal mix with its higher variance. Here, using the annual marginal mix instead of the hourly one leads to an underestimation of environmental benefits from PV-SC by between 10 and 25 %, depending on the impact category.

Based on the findings presented in this work it can be concluded that for technologies with varying load such as the assessed PV-SC installation, but also other technologies such as electric vehicles or stationary energy storage installations, the use of marginal electricity mixes will be increasingly relevant to their environmental assessment. Especially for bidirectional loads (storage systems), a good alignment of its operation with the hours of low and high marginal impact intensity can reap significant environmental benefits. As a consequence, this work provides updated inventory datasets for the average and marginal electricity mixes including a detailed consideration of imports from neighbouring countries. All underlying datasets, calculation tools and inventory tables are provided as supplementary data and can be readily re-used for follow-up life cycle assessment studies. Finally, developing the present approach further by incorporating also a predictive model allowing to consider future changes in the generation mix (done in a very simple way as an outlook in this work) imports would allow for even more comprehensive assessments of (future) energy technologies.

## Glossary

PV	Photovoltaics
PV-SC	Photovoltaic Self-Consumption
GWP	Global Warming impact Potential (climate change)
AP	Acidification impact Potential
FR	Use of Fossil Resources
MMR	Use of Mineral and metal Resources
NGCC	Natural Gas Combined Cycle
REE	Red Eléctrica de España (Spanish electricity grid operator)
LCA	Life Cycle Assessment

## CRediT authorship contribution statement

Jens F. Peters: Conceptualization, Methodology, Writing - Original Draft, Review & Editing. Diego Iribarren: Resources, Writing - Review & Editing, Validation; Pedro Juez Martel: Formal Analysis; Mercedes Burguillo: Resources.

## Data availability

The complete underlying data, inventory data files for direct import into openLCA and the supporting information to this manuscript is provided for download on Zenodo under doi:<https://doi.org/10.5281/zenodo.6652128>.

## 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 paper.

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## Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.scitotenv.2022.156963>.

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