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HAZARD STATEMENTS: LOOKING FOR ALTERNATIVES TO TOXICITY EVALUATION USING LCA

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ABSTRACT

Life Cycle Assessment is a methodology for the evaluation of potential hazards to the environment and to human health. It can be used for decision support when selecting materials for a product. It is a detailed method that can become very labor intensive. As alternatives, we introduce here two methodologies for ranking products and materials according to their safety: Both methods are built on two pieces of European legislation. *Hazard Traffic Lights* is a qualitative visual way to quickly identify potential hazards. *Total Hazard Points* is a quantitative method for weighting the different hazards related to a product. It is based on the method developed for the German Environmental Agency (UBA), but its scope includes all materials and hazards, rather than a selection of them.

As a case study we evaluated the 9 batteries described in the UBA study and compared our results with those presented there. In our opinion, batteries are in general terms more hazardous in the UBA study. This is due to more thorough identification of hazards—including some potentially more significant—and the inclusion of all the potential hazards of a material. Since not all the materials present in the battery were quantified, both sets of results should be considered an underestimation of the possible hazard.

KEYWORDS

Batteries, Hazard traffic lights, Methodology, Risk Assessment, Total Hazard Points

INTRODUCTION

Life Cycle Assessment (LCA) is an environmental management tool for the evaluation of products, processes, and services. It has a holistic perspective insofar as the whole life cycle of a product should be included—from cradle to grave—and all the relevant impacts—global warming, acidification, water use etc.—are taken into account [1–3]. The demanding task of constructing a complete Life Cycle Inventory (LCI), which identifies and quantifies those flows deemed of environmental importance has led to simplified LCAs. One such simplification is to reduce the boundaries of the system under study. Rather than cradle-to-grave, these studies are cradle-to-gate, gate-to-gate etc. Another simplification is the focus on a limited number of impacts, such as global warming [4] or water use [5].

A LCA-related tool combining both narrow boundaries and a single target impact is the Comparative Assessment of Toxic Emissions (CATE) [6,7]. In its most condensed version it can be used to rank bills of materials—or even single substances—according to their potential toxicity effects on human health or aquatic life.

Contrarily to most Life Cycle Impact categories, where only a handful of substances need to be taken into account, virtually every chemical can be considered toxic. Because of that, Life Cycle Impact Assessment methodologies (LCIA) devoted to toxicity—which are the basis for CATE— have an ever-expanding list of substances [8–10]. Still, LCA practitioners have had to calculate toxicity potentials—or characterization factors (CFs)—for substances they considered relevant in their studies [11,12]. The addition of new substances has become easier with the newest version of USEtox. USEtox 2.0 also includes emissions compartments such as household and industrial indoor air, closing the gap between LCA and Risk Assessment (RA).

The growing concern about environmental and health safety worldwide, has resulted in a number of pieces of legislation on the subject. One in particular, the REACH regulation [13], has made freely available most of the information an LCA practitioner needs to calculate CFs for new substances. Still, that information is not always available and even when it is, a CATE might be considered too labor intensive.

Here we propose two straightforward methodologies for the comparison of chemical substances, the first a qualitative method first used by the authors in [14] but not fully described. The second is an adaptation of a quantitative method first presented by the German Environmental Agency (*Umwelt Bundesamt, UBA)* [15]. Both are based on EU legislation [16,17] and information made consequently available. As electrochemical energy storage is our main area of research, the examples presented here are batteries, but the methodology can be easily applied to any other bill of materials.

METHODOLOGIES

1. Hazard traffic light (HTL)

The regulation of the European Parliament on classification, labeling, and packaging (CPL) [16], based on the United Nations' Globally Harmonized System (GHS) [18] guarantees that the hazards presented by chemicals are clearly communicated to their users in the EU. Substances and mixes are classified according to the identified hazards, which are communicated through standard statements and pictograms (www.echa.eu). Hazard statements include a hazard class (the nature of the physical health or environmental hazard, e.g. flammable, acute toxicity if swallowed, chronic toxic to aquatic life, etc.) and the hazard category (the severity). Further information includes a hazard pictogram and a signal word: "Danger" for the more severe hazard category, and "Warning" for the less severe ones [16].

Each hazard statement has a code of the form Hxxx, e.g. H220, for *extremely flammable;* H303, *may be harmful if swallowed*; or H412, *harmful to aquatic life with long lasting effects.* All physical hazard statements have an H2xx code, health hazard statements a H3xx, and environmental hazards a H4xx. The second figure in the code usually indicates the hazard class, e.g. H30x corresponds with acute toxic if swallowed, and H40x with toxic to aquatic life. However, this is not always the case, as the flammable hazard class includes the statements from H220 to H231. The last figure of the code identifies a specific hazard statement within a class, e.g. H300 corresponds to "Fatal if swallowed" while H303 stands for "May be harmful if swallowed" [16]. As in the example, higher numbers within a class tend to indicate a reduction of its hazardousness.

Hazard labeling can be used to compare substances by their hazardousness, which in turn can be used as a screening procedure for material selection. The 62 hazard statements offer a finite number of indicators that can be grouped into 28 hazard classes and broadly divided by their signal word—some hazard statements can have both or none. By comparing the number, class, and category of the hazard statements of two or more chemicals, it is possible to select the one that is perceived to be as less harmful (Table 1).

Table 1 Hazard traffic light classification

Physical hazards	Explosives		H200	H201	H202	H203	H204	H205	H206
	Flammable	gas	H220	H221					
		aerosol	H222	H223					
		liquid	H224	H225	H226				
		solid	H228						
	Oxidizing gas		H270						
	Gas under pressure		H280	H281					
	Self-reactive substances and mixtures Organic peroxides		H240	H241	H242				
	Pyrophoric	liquid solid	H250						
	Self-heating substances and mixtures		H251	H252					
	Substances and mixtures which in contact		H260	H261					
	Oxidizing	liquid solid	H271	H272					
	Corrosive to metals		H290						
Health hazards	Acute toxicity	Oral	H300	H301	H302				
		Dermal	H310	H311	H312				
		Inhalation	H330	H331	H332				
	Skin corrosion/ irritation		H314	H315					
	Serious eyes damage/eye irritation		H318	H319					
	Respiratory or skin sensitization		H334	H317					
	Germ cell mutagenicity		H340	H341					
	Carcinogenity		H350	H351					
	Reproductive toxicity		H360	H361	H362				
	Specific target organ toxicity-single exposure		H370	H371	H335	H336			
	Specific target organ toxicity-repeated exposure		H372	H373					
	Aspiration hazard		H304						
Env.	Hazardous to the aquatic environment	Acute	H400						
		Chronic	H410	H411	H412	H413			

Danger   Warning   No hazard word

The first step is to identify the different hazards a substance might present. These commonly appear in Material and Safety Datasheets facilitated by the chemical's supplier. Additional information can be found on the webpage of the European Chemistry Association (www.echa.eu).

Once identified, we suggest creating a table like Table 1, using red to indicate hazards with the word "Danger," yellow for those with "Warning," and gray for those without a hazard word. It should be stressed that this is a qualitative method: two "Warnings" do not make "Danger". Also, the regulation's procedures exclusively indicate which substances should be classified as hazardous. Statements like "non-toxic" or "non-hazardous" are inconsistent with the regulation and as such, should not be used to label—or compare—a substance. Thus, in this traffic light system there is no green sign, unlike the first iteration of this methodology [14], and hazards not reported for a given substance are left blank.

It is suppliers—producers, importers, etc. — who evaluate the potential risks of their chemicals to human health and the environment before placing them on the market. They are also responsible for classifying and labeling their products, which might lead to discrepancies—i.e. the same substance might have different hazard statements depending on the supplier. As such, when hazards of the same class with the "Danger" and "Warning" words are reported for a substance—e.g. H301 *Toxic if swallowed (Danger)* and *H302 Harmful if swallowed (Warning)*—we use both yellow and red for this hazard class.

In certain cases, the decision on the classification of a substance is taken at EU level and suppliers must apply this harmonized classification and labeling. Harmonization often concerns the most hazardous substances: carcinogenic, mutagenic, toxic for reproduction, or respiratory sensitizers (www.echa.eu). If a hazard has been harmonized for a certain substance and similar hazards have been reported, only the harmonized variation will be taken into account. Following the previous example, if both H301 and H302 are reported in a substance and the latter has been harmonized, only H302 will be taken into account.

As an example, we will explain how to create the HTL of lithium. Its CPL webpage on the ECHA site (https://echa.europa.eu/information-on-chemicals/cl-inventory-database/-/discli/details/13762) mentions two harmonized hazard statements:

- H260 In contact with water releases flammable gases which may ignite spontaneously.
- H314 Causes severe skin burns and eye damage.

Harmonized statements can confidently be added to the HTL, since they will take precedence over other statements of the same class (Table 2).

In addition, some suppliers have reported following additional hazards:

- H301 Toxic if swallowed
- H318 Causes serious eye damage
- H228 Flammable solid
- H413 May cause long lasting harmful effects to aquatic life.

Since each of these hazards corresponds to a different class, there are no conflicts between them, or with the harmonized hazards, and thus they can be added to the HTL (Table 3).

Table 2 Hazard Traffic Light of Lithium: harmonized hazards

Physical hazards	Explosives		
	Flammable	gas	
		aerosol	
		liquid	
		solid	
	Oxidizing gas		
	Gas under pressure		
	Self-reactive substances and mixtures Organic peroxides		
	Pyrophoric	liquid	
		solid	
	Self-heating substances and mixtures		
	Substances and mixtures which in contact with water emit flammable gases		H260
	Oxidizing	liquid	
		solid	
	Corrosive to metals		
Health hazards	Acute toxicity	Oral	
		Dermal	
		Inhalation	
	Skin corrosion/ irritation		H314
	Serious eyes damage/eye irritation		
	Respiratory or skin sensitization		
	Germ cell mutagenicity		
	Carcinogenity		
	Reproductive toxicity		
	Specific target organ toxicity-single ex.		
	Specific target organ toxicity-repeated ex.		
	Aspiration hazard		
Env.	Hazardous to the aquatic environment	Acute	
		Chronic	

Table 3 Complete Hazard Traffic Light of Lithium

Physical hazards	Explosives		
	Flammable	gas	
		aerosol	
		liquid	
		solid	H228
	Oxidizing gas		
	Gas under pressure		
	Self-reactive substances and mixtures Organic peroxides		
	Pyrophoric	liquid	
		solid	
	Self-heating substances and mixtures		
	Substances and mixtures which in contact with water emit flammable gases		H260
	Oxidizing	liquid	
		solid	
	Corrosive to metals		
Health hazards	Acute toxicity	Oral	H301
		Dermal	
		Inhalation	
	Skin corrosion/ irritation		H314
	Serious eyes damage/eye irritation		H318
	Respiratory or skin sensitization		
	Germ cell mutagenicity		
	Carcinogenity		
	Reproductive toxicity		
	Specific target organ toxicity-single ex.		
	Specific target organ toxicity-repeated ex.		
	Aspiration hazard		
Env.	Hazardous to the aquatic environment	Acute	
		Chronic	H413

UBA methodology

As part of the German energy transition, the UBA published a report where a number of energy storage technologies where evaluated according to several environmental criteria. One such was the ranking of several batteries based on the hazard statements of the materials they contained [15].

The most vital information required to evaluate those batteries was their bill of materials, that is, a detailed description of the chemicals it contains and the amounts to which they are present. In the example in Figure 1, the different substances are denoted with capital letters (A, B, C, etc.) and their masses as m_i (m_a, m_b, etc.). Because the batteries evaluated have very different characteristics, namely different specific energies (Wh/kg), a common reference was necessary to compare them. This reference is the energy stored in each battery, measured in kWh (E kWh for the example battery in Figure 1).In this way, batteries of different sizes can be compared without artificially penalizing the larger ones.

As in HTL, it is necessary to identify the potential hazards associated with each material present in the battery (e.g. in Figure 1 material A is associated with hazards HXX1 and HXX2). After that, hazards are ranked according to the directive 2012/18/EU [17] on the control of major-accident hazards involving dangerous substances. This piece of legislation defines when a location where chemicals are stored requires a major accident prevention policy (MAPP). This will depend on whether or not certain tonnages exceed a lower or an upper tier, which varies among the different categories of dangerous substances. The UBA methodology classifies hazards according to these lower tiers (LT). For a given substance, the minimum of all its LTs is chosen, as it defines its greatest hazard (min(LT_i) in Figure 1).This is because LTs are measured in metric tons—of hazardous material that can be stored without implementing a MAPP—and thus a lower value indicates a bigger hazard. Not all hazards have an LT in the EU directive, and thus those hazards are not taken into account.

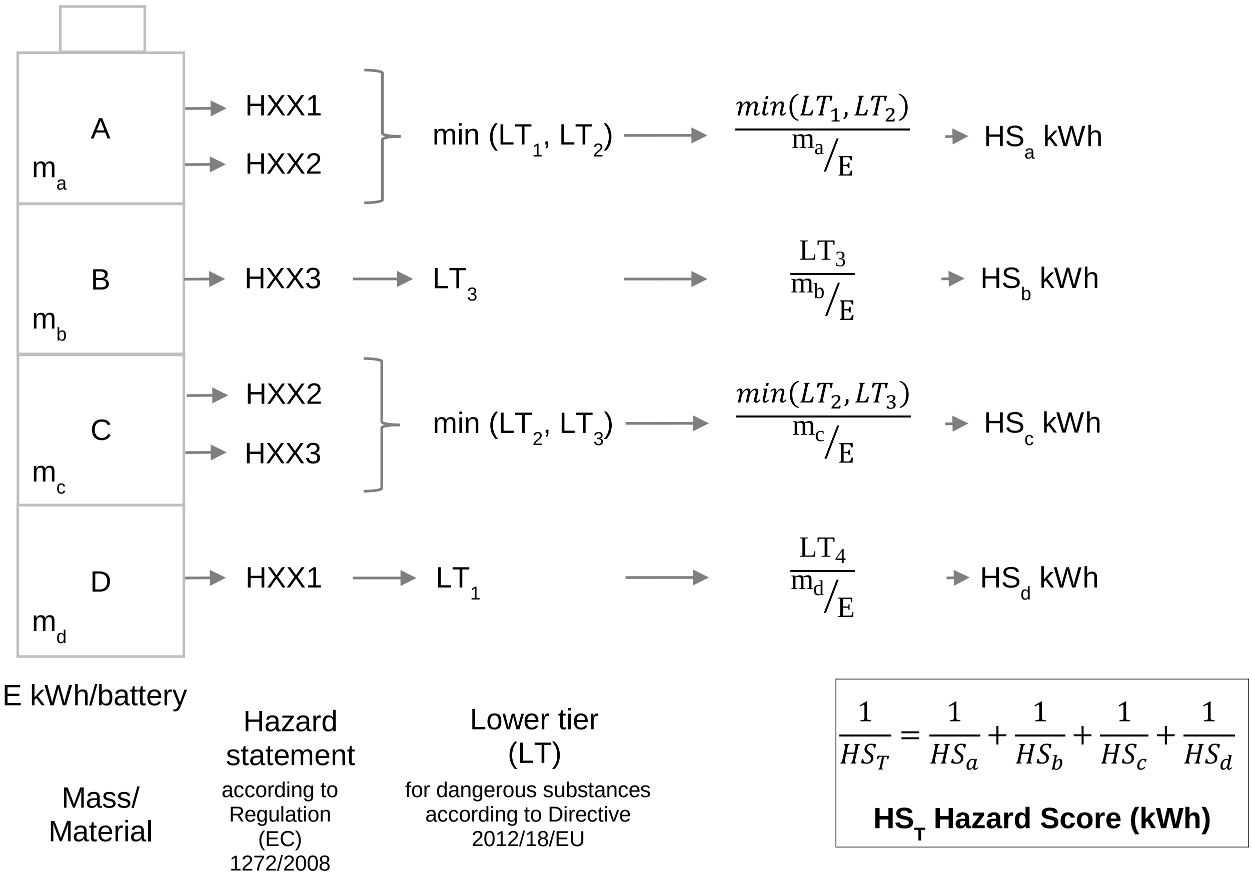


Figure 1 UBA methodology

Since the UBA methodology was designed for the comparison of batteries, its final score is expressed in kWh. This allows the comparison of batteries of different sizes and characteristics. Thus, if *m* grams of material *M*—whose hazards have a lower tier of LT_1, LT_2, *and* LT_3—in a battery storing E kWh, the hazard score (HS) of that material is as per equation 1.

$$HS_M(kWh) = \frac{min(LT_1, LT_2, LT_3)t}{\mathrm{m_M}g/_{E\ kWh}} \times \frac{10^6 g}{t} \quad (1)$$

If the battery is composed of several hazardous materials, then reciprocal total hazard score of the battery is the sum of the reciprocate of the individual hazards as per equation 2.

$$\frac{1}{HS_T} = \sum_{i}^{n} \frac{1}{HS_i} \quad (2)$$

The final result can be interpreted as the amount of energy that can be stored using a given battery technology without having to apply an MAPP. Still, the results are not absolute, meaning that batteries with similar scores are considered of the same level of hazard (++, +, 0, - or --). An additional highlight is given to those batteries using carcinogenic, mutagenic or toxic to reproduction (CMR). Batteries with CMR substances are demoted one category, e.g. a “++” battery with a CMR substance becomes a “+” battery.

2. Proposed changes to the UBA Methodology: Total hazard points (THP)

The major benefit of the UBA methodology compared to the one we presented earlier is its quantitative approach. Two simple calculations give mathematical support for the ranking of different materials. The method we described earlier does not support quantitative ranking, but it offers more detailed information on the hazards a material might pose. Hence, we encourage the use of both methodologies combined. Nevertheless, it is our opinion the UBA methodology presents two significant drawbacks derived from the use of Directive 2012/18/EU:

1. It reduces a material to a single hazard. While this might make sense from a policy perspective—its objective being to establish whether or not a MAPP needs to be implemented—it hinders any classification, as it diminishes the danger of any substances with more than one potential hazard.
2. The absence of reference quantities—LTs—for a number of hazards might also diminish the danger of certain substances.

We propose therefore an alternative method to rank materials—and batteries—based on the UBA one, as an attempt to overcome the aforementioned limitations (Figure 2).

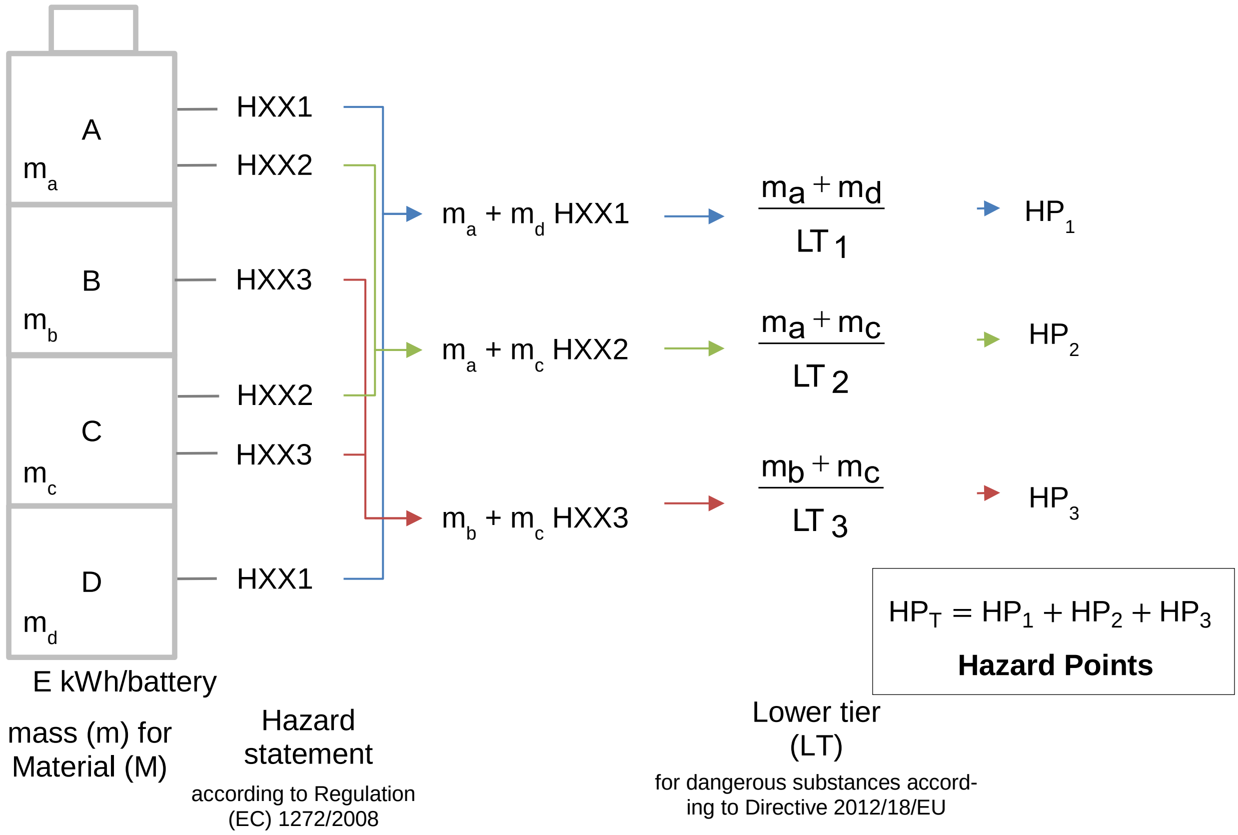


Figure 2 Alternative to the UBA method

By including all potential hazards of a substance, the focus of the assessment shifts from materials—the case of UBA—to hazards. As a consequence, after identifying the hazards of the materials comprising the product under assessment, it is possible to add the mass of each material causing a given hazard H (Equation 3). The methodology is unit independent, but to obtain comparable results consistency within and without the product should be kept. In the case studies presented later, we will use grams as reference—hence the hazard points will be indicated as HP(g).

$$m_H = \sum_{i}^{n} m_i H \quad (3)$$

The inclusion of additional hazards to the UBA methodology is necessarily subjective, as the Directive 2012/18/EU does not offer LTs form them. It does offer however LTs for a number of named dangerous substances: ammonium nitrate, sulfur trioxide, etc. Based on these substances, their hazards, and their LTs we developed the following rules to give all missing hazards an LT:

1. Only the LTs of Part 1 of Annex I of Directive 2012/18/EU “Categories of dangerous substances”—5, 10, 50,100,150,200 and 5000 metric tons—are used. In this way, huge disparities with the UBA method are avoided. However, it might also reduce the risk perception of very dangerous substances, as very low LTs—0.1, 0.2, etc.—are not used.
2. For a given hazard category, all hazards bearing a “Danger” signal word will have the same LT. The same applies for hazards with the “Warning” signal word or no signal word. If for this hazard category there is a hazard with the “Warning” signal word, its LT will be one level higher (e.g. a “Danger” with an LT of 10 metric tons becomes a “Warning” of 50 tons).
3. If a hazard does not have a signal word, it will take the lowest LT within its category. This is consistent with H206, which has the same LT as the “Danger” hazards of the explosive category.
4. If a hazard has both the “Danger” and “Warning” signal words, then, for the purposes of Rule 3, it is considered a “Danger” hazard. This is a conservative approach consistent with H272—who has the same LT as the “Danger” hazard of its category—but not with H242—who has a higher LT than the “Danger” hazard of its category.

According to these criteria, the following LTs are considered:

5. Substances and mixtures which in contact with water emit flammable gases: H261 (LT 100 metric tons).
6. Specific target organ toxicity—single exposure: H371, H335 and H336 (LT 100 metric tons).
7. Hazardous to the aquatic environment (Chronic): H412 and H413 will have both an LT of 200 metric tons, as for H411.
8. Acute toxicity (dermal): H331 (LT 50 metric tons)
9. Acute toxicity (all): For H302, H312, and H332 an LT of 100 metric tons is assumed.

In order to assign an LT to other hazards, additional assumptions are required. Whenever possible, these LTs are backed by substances with harmonized hazards sentences appearing in Part 2 of Annex I of Directive 2012/18/EU.

1. Gas under pressure. Several gases under pressure appear in Part 2, but none of them have sentences H280 or H281. Because this hazard will usually appear with more dangerous hazards (e.g. flammable gas), we designated the highest LT, 5000 metric tons, to it.
2. Corrosive to metals. Hazard sentence H290 was not reported for any substance in Part 2. Rather than not allotting an LT to it, we allocated the highest LT, 5000 metric tons to it.
3. Self-heating substances and mixtures. No substance in Part 2 had hazard sentences H251 or H252. We allocated the same LTs as those for self-reacting substances, 10 and 50 metric tons respectively.

4. Skin corrosion/irritation. A large number of substances from Part 3 corrode or irritate the skin, with LTs from 0.2 to 2 metric tons for H314. We assigned an LT of 10 tons to H314 and, according to Rule 3, an LT of 50 tons to H315.
5. Serious eye damage/eye irritation. The LTs for substances with H319 range from 5 to 500 metric tons. Thus, we allotted an LT of 50 tons for H319 and, following Rule 3, an LT of 10 metric tons for H318. Based on this, we assigned an LT of 100 tons to H319 and, according to Rule 3, an LT of 50 tons to H334.
6. Respiratory or skin sensitization: Substances with the hazard statement H317 range from a UT of 0.15 metric tons to a LT of 500 tons.
7. Germ cell mutagenicity: Three substances—ethylenemine, ethylene oxide, and propylene oxide—with LTs of 10, 5, and 5 metric tons respectively—have been identified as potential mutagenic (H340). Based on this, we gave H340 an LT of 5 tons and, according to rule #3, an LT of 10 tons to H341.
8. Carcinogenity: A number of substances from Part 2 had been reported as potential carcinogen (hazard sentence H350). These substances with LTs ranging from 0.5 to 10 metric tons. Following Rules 2 and 3, we assigned LTs of 5 and 10 tons to H350 and H351 respectively.
9. Reproductive toxicity. Methylisocyanate, with an UT of 0.15 metric tons, is the only substance from Part 2 with a hazard from this category (H362). Based on this, and to be consistent with Rules 2 and 4, a LT of 5 metric tons is assumed for H360 and H362.Following Rule 3, H361 has a LT of 10 metric tons.
10. Specific target organ toxicity-repeated exposure. These substances are considered to be less hazardous than those under “single exposure”. Thus, LTs of 100 and 200 metric tons are assigned to H372 and H372 respectively.
11. Aspiration hazard: No substances with hazard sentences H304 appear in Part 2. As a proxy, we allot the same LT as that of H334 “Respiratory or skin sensitization”: 50 metric tons.

All the LTs, calculated or taken directly from the bibliography are presented in Table 4

Table 4 Reference Quantities (Lower tiers, LT, in metric tons) for the hazard sentences. Based on [17]. Figures in italics were assigned by the authors as explained in the manuscript.

Physical hazards	Explosives		H200 10	H201 10	H202 10	H203 10	H204 50	H205 10	H206 10
	Flammable	gas	H220 10	H221 10					
		aerosol	H222 150	H223 150					
		liquid	H224 10	H225 5000	H226 5000				
		solid	H228 50						
	Oxidizing gas		H270 50						
	Gas under pressure		H280 *5000*	H281 *5000*					
	Self-reactive substances and mixtures Organic peroxides		H240 10	H241 10	H242 50				
	Pyrophoric	liquid solid	H250 50						
	Self-heating substances and mixtures		H251 *10*	H252 *50*					
	Substances and mixtures which in contact with water emit flammable gases		H260 100	H261 100					
	Oxidizing	liquid solid	H271 *50*	H272 *50*					
	Corrosive to metals		H290 *5000*						
Health hazards	Acute toxicity	Oral	H300 5/50	H301 50	H302 *100*				
		Dermal	H310 5/50	H311 50	H312 *100*				
		Inhalation	H330 5/50	H331 50	H332 *100*				
	Skin corrosion/ irritation		H314 *10*	H315 *50*					
	Serious eyes damage/eye irritation		H318 *10*	H319 *50*					
	Respiratory or skin sensitization		H334 *50*	H317 *100*					
	Germ cell mutagenicity		H340 *5*	H341 *10*					
	Carcinogenity		H350 *5*	H351 *10*					
	Reproductive toxicity		H360 *5*	H361 *10*	H362 *5*				
	Specific target organ toxicity-single exposure		H370 50	H371 *100*	H335 *100*	H336 *100*			
	Specific target organ toxicity-repeated exposure		H372 100	H373 *200*					
	Aspiration hazard		H304 50						
Environ. hazards	Hazardous to the aquatic environment	Acute	H400 100						
		Chronic	H410 100	H411 200	H412 *200*	H413 *200*			

Danger   Warning   No hazard word

CASE STUDY

The nine batteries evaluated in the UBA report [15] are used here to illustrate the use of the two methodologies developed. In bold, the final score given in the UBA report, from worst **--** to best **++ (**Table 5**)**.

Table 5 Batteries included in the UBA study

Group	**Name**	**UBA score**
Lead-acid battery	Lead-acid	**--**
Lithium ion batteries (LIB)	Lithium nickel manganese cobalt oxide cathode and carbon anode (C-NMC)	**--**
	Lithium Nickel Cobalt Aluminum oxide cathode and carbon anode (C-NCA)	**+**
	Lithium iron phosphate cathode and carbon anode (C-LFP	**++**
	Lithium iron phosphate cathode and lithium titanium oxide anode (LTO-LFP)	**+**
Redox flow batteries	Vanadium-vanadium (V-V)	**0**
	Chromium-iron (Cr-Fe)	**++**
Non-lithium batteries	Sodium-sulfur (Na-S)	**0**
	Zinc-air (Zn-air)	**0**

A relatively large number of substances were identified for each battery, but few of them were taken into account by the UBA to rank the technologies. For the sake of brevity consistency with the results presented in [15], we only evaluated the short list of materials for each battery. Nevertheless, it is our impression that the UBA report does not take into account all the potential hazards associated with these materials. While that might have few consequences for their method—only one hazard is required per material—it will have an impact in the methodologies we present, as we aim to cover the full array of possible hazards.

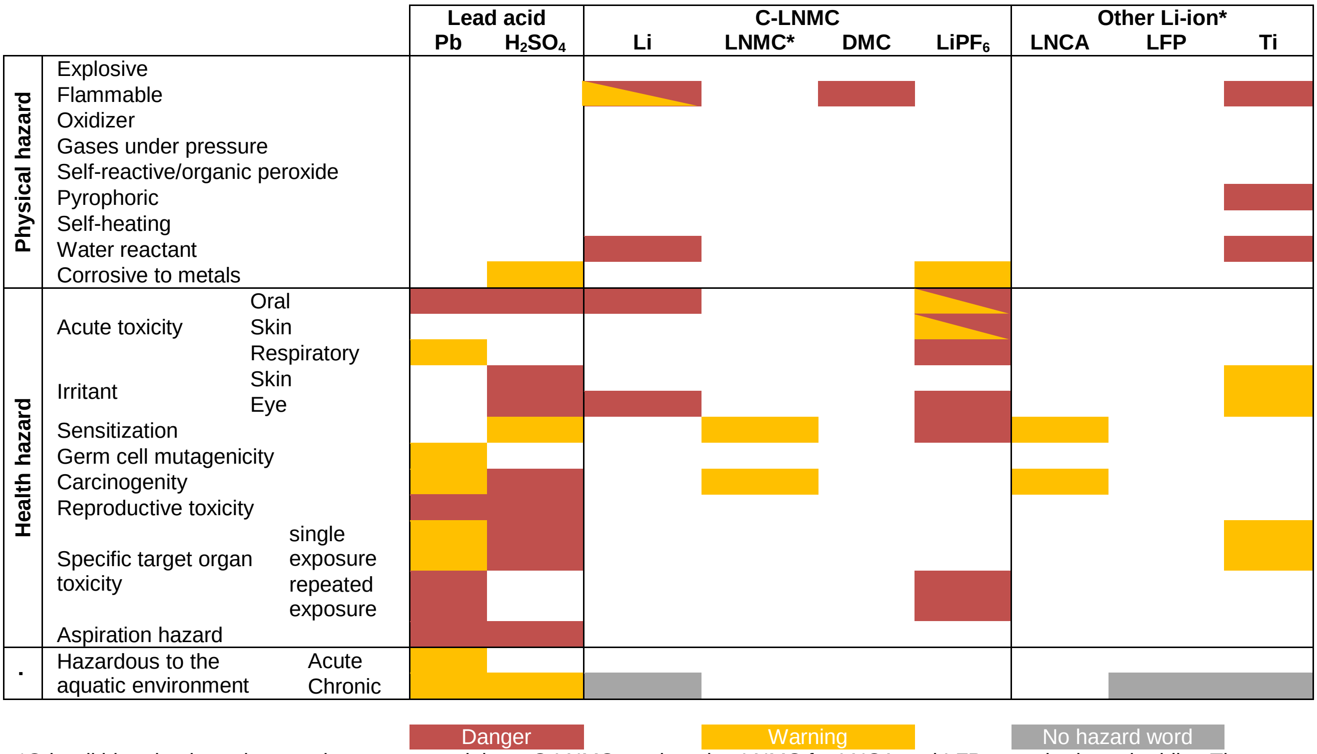
1. Hazard traffic light

One of the first things that become apparent when glancing at the results presented in Tables 6to 8 is that this methodology is probably better suited for comparison of individual materials with a similar function, as we did in [14], rather than to entirely different batteries. Since there is no weighting, batteries requiring a variety of materials like Cr-Fe or Zn-air, might seem to be more harmful than batteries where fewer materials are evaluated, like V-V or Na-S respectively (Tables 7 and 8).

Still, valuable information can be extracted from these tables. Lead acid batteries, despite using only two key materials, are revealed as probably one of the least safe alternatives (Table 6). Table 1 also suggests there are relatively few differences between LIBs when it comes to safety: LNMC and LNCA present exactly the same risk profile, and LFP does not alter the profile significantly. The use of Ti as anode does not seem justified in safety terms, as it is a substance associated with a variety of risks. However, it is necessary to mention that graphite, the anode used in the other three LIB is not presented in these results.

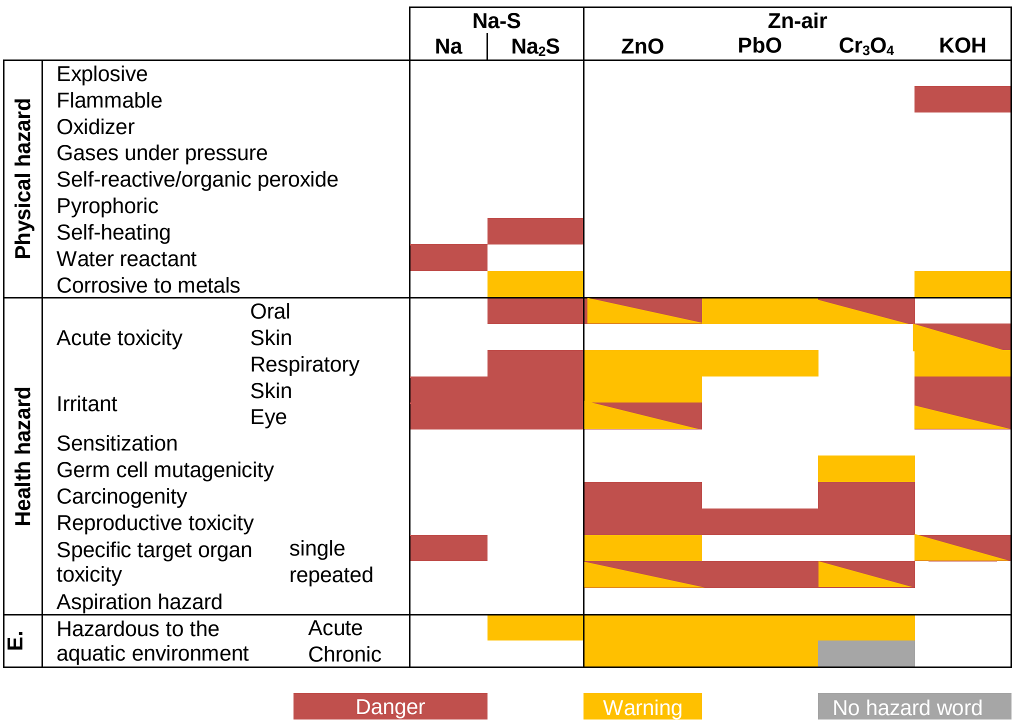
The results presented in Tables 6 to 8 highlight that, in general terms, the materials used for the production of batteries are most harmful to human health. Only a minority of materials may cause some physical damage, usually corrosion to metals. Damage to the aquatic environment falls somewhere between those two groups, all batteries evaluated pose a threat to the environment, but lead-acid and Zn-air might be particularly harmful.

Table 6 Hazard traffic light of Lead acid and Lithium ion batteries



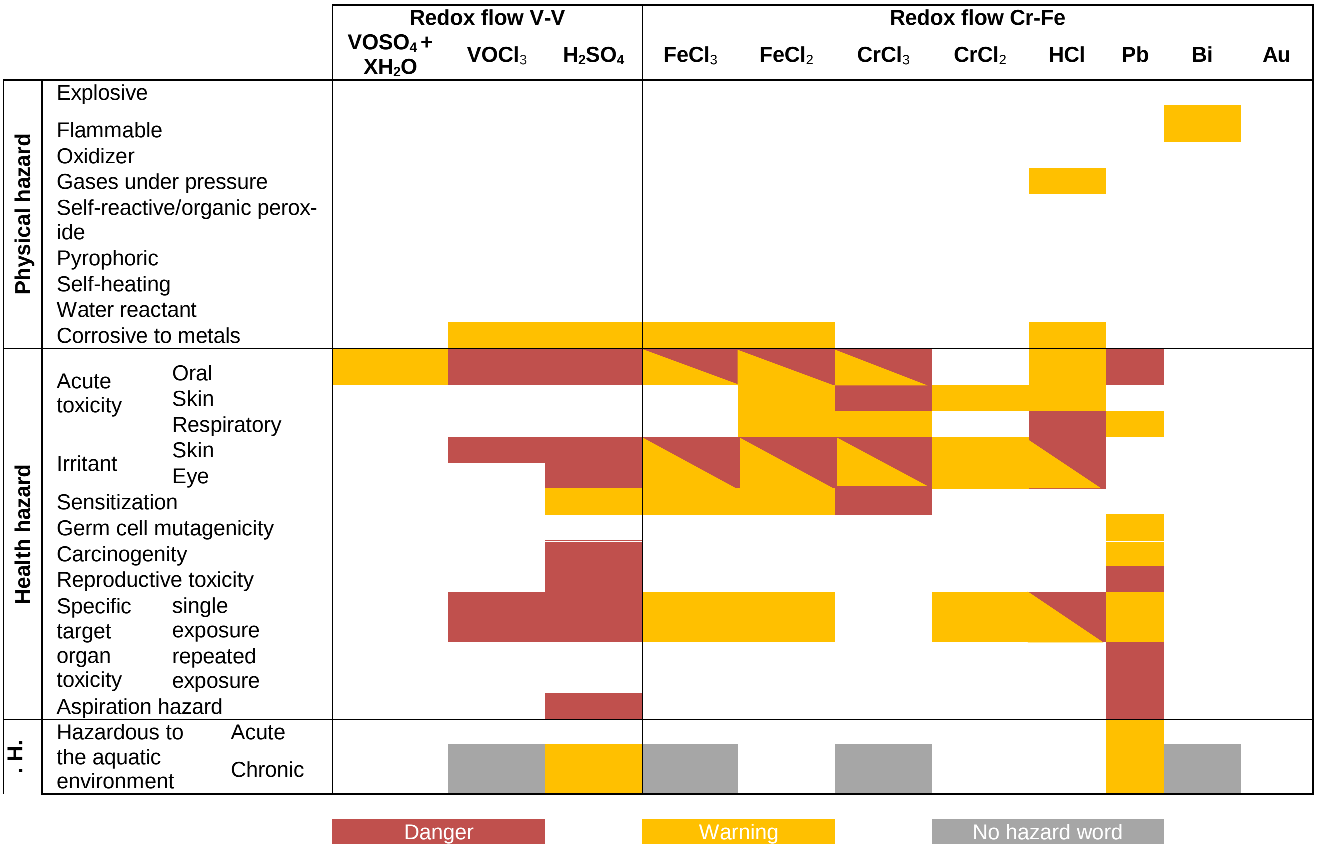
*Other lithium-ion batteries use the same materials as C-LNMC, exchanging LNMC for LNCA and LFP as cathode and adding Ti as anode.

Table 7 Hazard traffic light of non-lithium batteries



When assessing the potential damages to human health, it is possible to observe a wide variety of effects. All batteries but Na-S had at least one substance affecting the main hazard categories—acute and target organ toxicity, irritation/sensitization and CMR. None of the materials assessed were reported to cause aspiration hazards and for one substance, gold, no hazards had been identified. Looking at the individual kinds of batteries, lead acid seems to be particularly hazardous in terms of CMR and target organ toxicity. LIBs seem to be the least harmful to human health, most of their impacts being in the area of acute toxicity. Na-S seems especially dangerous because of the irritants it contains, while Zn-air and the redox-flow batteries wholly cover the full array of potential hazards to human health.

Table 8 Hazard traffic light of redox flow batteries



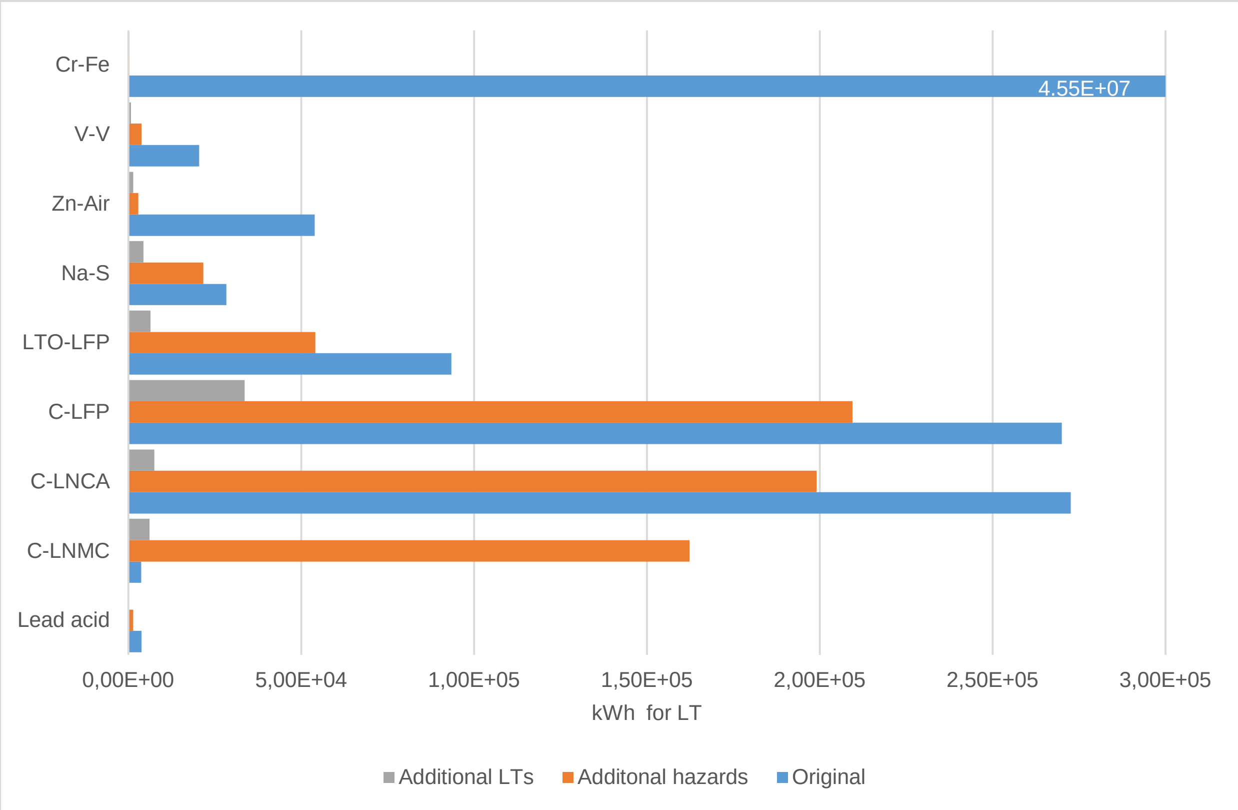
2. UBA methodology vs THP. A two-step comparison

The UBA and the THP methods have two different ranking philosophies. While the first only takes into account one hazard per substance, the second one aspires to cover all hazards that can be related to a material. As a result, any comparison between them, other than the actual ranking of the batteries, will not have much meaning. Nevertheless, it is possible to include parts of the THP to the UBA methodology for better appreciation of their differences.

Not all hazards reported by supplying companies to the ECHA were mentioned in the UBA report. Thus, it is possible the results there presented are underestimating the hazard of the batteries evaluated. In the first step, we recalculated the hazard score of each battery (as kWh needed to reach LT) using when necessary a hazard not included in the UBA report but for which there was an LT defined in Directive 2012/18/EU [17]. Those results can be seen in Figure 3 (blue vs. orange bar). Such a comparison shows the effect of looking for the worse hazard, without adding the subjectivity of the LTs we allocated to additional hazards. The effect of the *new hazards with their new LTs* can also be seen in Figure 3 (blue vs. grey).

For both comparisons, the most obvious change in scores is for Cr-Fe. In the original results, it was ranked among the best alternatives, capable of storing more than 45 million kWh before reaching LT. Using additional hazards and LTs, it becomes the one with the lowest score (16.5

kWh) and arguably the most hazardous battery. This is not because the only substance used to calculate the hazard score of this battery now has a hazard with a lower LT—Pb, with H410 (LT 100) is now an H301 (LT 50)—but because most of the substances of this battery where not included for the calculation of the hazard score—namely Cr and HCl. This dramatic change high-



lights the need for including all substances in a battery, particularly those used in large quantities.

Figure 3 Effect of using additional hazard statements and additional LTs in the UBA methodology

C-LNMC is the only battery becoming less hazardous when using Directive LTs (Figure 3, orange bars and 9). NMC is responsible for this change. The UBA report does list this substance as “Fatal if inhaled” (H330), but none of the suppliers reported the hazard to the ECHA. The other eight batteries present important reduction in their scores, suggesting that they are more hazardous than initially reported. The score of Zn-air is 19 times lower than before—and thus 19 times more hazardous. Even substances ranking better than before, such as C-LFP, scored lower—29% less. These score reductions stress the importance of identifying all the pertaining hazards, as it is possible that all suppliers report those with lower LTs.

The use of hazards without LTs in Directive 2012/18/EU [17] dramatically reduces the scores of all batteries but C-LNMC—NMC is reported to be carcinogenic (H351), but the LT that we allocated for this hazard is lower than for H330—and Cr-Fe—whose score is almost identical to the one obtained with the addition of new substances and hazards. For the other batteries, the scores are between 6.5 and 36 times lower than the original—for Na-S and C-LNCA respectively. Calculating the score using hazards with our own LTs clearly had an impact on the ranking of the batteries (Table 6), particularly H314 (LT10). While it would be possible to argue that this LT—or any other—is too low, it is worth mentioning that similar hazards appeared in every battery but Cr-Fe and Zn-air. Nevertheless, this comparison demonstrates the need for LTs for every hazard, since otherwise it is likely that we would underestimate the hazard of a product. A consensus between hazard experts in allocating LTs for the hazards we did in this study is highly desired.

Table 9 UBA battery ranking: original ranking based on KWh/LT, and using additional hazard statements and additional LTs

Original ranking		Additional hazards	Additional LTs
--	C-LNMC	Cr-Fe	Lead acid
	Lead acid	Lead acid	Cr-Fe
	V-V	Zn-Air	V-V
0	Na-S	V-V	Zn-Air
	Zn-Air	Na-S	Na-S
+	LTO-LFP	LTO-LFP	C-LNMC
+	C-LFP	C-LNMC	LTO-LFP
++	C-LNCA	C-LNCA	C-LNCA
++	Cr-Fe	C-LFP	C-LFP

3. Total Hazard Points

We present a detailed example of the use of THP for 1 kWh lead acid battery in Table 10, prior to a comparison of the 9 batteries evaluated (Figure 4). The UBA report identified five hazardous substances in a lead-acid battery, but PbO, PbO_2 and Sb were not quantified. Thus, only Pb and H_2SO_4 could be used to calculate the total hazard points. The suppliers of these two materials identified 9 and 11 hazards respectively for a total of 21 different hazards—both substances are toxic if swallowed (H301) and may target specific organs after repeated exposure (H372).

HTL already suggested this battery was harmful to both the environment and human health. However, once the hazards are quantified, most of the impact is related to the latter group. The impacts are evenly distributed between the two substances: Pb is responsible for almost 77% of the total hazard points, but it also accounts for almost 76% of the mass considered here.

Three impacts for each substance—H341 (suspected mutagenic), H351 (suspected carcinogenic) and H360 (reproductive toxicity) for Pb; H314 (skin corrosive), H318 (eye damage) and H350 (carcinogenic) for sulfuric acid—account for more than 80% of the hazard points, suggesting that hazards in a substance might follow the Pareto principle. This demonstrates that reducing one substance to a single impact might seriously underestimate its hazards. However, it also suggests that it might not be necessary to account for all the hazards of a material. In the absence of a general rule for the selection of important hazards, we still recommend to evaluate all of them.

Table 10 Calculation of Total Hazard Points for a 1kWh lead-acid battery

			Pb	H_2SO_4	Total
		g/kWh	26235	7900	34135
		LT		**HP(g)/kWh**	
Phy. H.	H272	50		158	158
	H290	5000		1.58	1.58
	Subtotal		*0*	*159.58*	*159.58*
Human health Hazard	H301	50	524.7	158	682.7
	H312	100		79	79
	H314	10		790	790
	H318	10		790	790
	H332	100	262.35		262.35
	H335	100		79	79
	H341	10	2623.5		2623.5
	H350	5		1580	1580
	H351	10	2623.5		2623.5
	H360	5	5247		5247
	H370	50		158	158
	H371	100	262.35		262.35
	H372	100	262.35	79	341.35
	Subtotal		*11805.8*	*3713*	*15518.8*
Env. Haz.	H400	100	262.35		262.35
	H410	100	262.35		262.35

	H412	200		39.5	39.5
	Subtotal		*524.7*	*39.5*	*564.2*
	TOTAL HP(g)		**12330.5**	**3912.08**	**16242.5**

Figure 4 shows the total hazard points for the batteries evaluated. As previously mentioned, all calculations were made using grams for the different masses, thus these hazard points are on a scale of grams—HP(g). Also, because the amount of material used was referred to as g/kWh, the final result is also per kWh of energy stored. This allows a direct comparison between batteries.

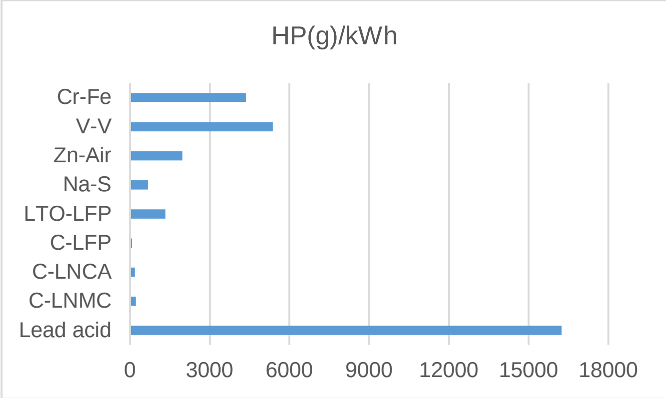


Figure 4 Total Hazard points (grams) per kWh stored in the different batteries evaluated

As with the UBA method with additional LTs, when using THP C-LFP is the least hazardous battery, followed again by C-LNCA. As a group, LiB could be considered the safest, but important differences can be observed between them. As mentioned before, the fact that the carbon anode—and other materials—are not accounted for, underestimates the impacts of these batteries. If, to be consistent with the rest of the LIB, we exclude the TiO anode from the LTO-LFP battery, its results would have been closer to the rest of the LIB.

Lead-acid continues to be the most harmful battery—the causes been already explained—followed by the redox-flow batteries V-V and Cr-Fe. These two batteries share with Lead-acid a low energy density in comparison with LIB and others—at least according to [15]. They need large quantities (10l or more) of acid to store 1 kWh —H_2SO_4 in case of V-V and HCl in case of Cr-Fe—which accounts for the majority of the hazard points—94% for V-V and 64% for Cr-Fe. These results highlight two ways to achieve safer products—batteries or others. One is the use of less harmful materials. The other is to increase the efficiency—energy density in the case of batteries—of the product even if it means using more hazardous materials.

CONCLUSIONS

We presented here two methods for the evaluation of materials and products according to their hazard potential: Hazard Traffic Lights (HTL) and Total Hazard Points (THP), both based in European legislation [16,17].

HTL has proved to be a quick visual alternative for the identification of hazards. It can be easily applied for a qualitative comparison of materials with similar functions. However, we do not recommend its use for the comparison of different products. It might be difficult to balance products with a few very hazardous materials and products with a large number of materials—even if those are only mildly hazardous.

THP is a quantitative method for weighting the different hazards related to a product. It is based on the method developed for the German Environmental Agency (UBA) [15], but its scope include all materials and all hazards rather than a selection of them. Therefore, THP could be used in the future for a more complete estimation of potential hazard impacts. Nevertheless, by comparing these two methods we wanted to stress the importance of identifying all the potential hazards of a material—even if only one hazard per material is going to be used in the evaluation—and the necessity of ranking all hazards, whether using existing references or an ad hoc system like the one we developed here.

The case study, a comparison of 9 batteries presented in an UBA report [15] was limited due to the absence of a detailed composition of the batteries. While we think it is enough to introduce both methodologies, the results obtained should only be considered as indicative when selecting a battery.

It is necessary to stress that all three methods mentioned here evaluate the hazards of the materials of a product, a battery, not the hazards of the product itself. Some hazards cannot be applied to the materials in the batteries because of their state—e.g. the HCl in a Cr-Fe redox-flow battery is liquid [19] and thus H280 "Gas under pressure" should be of little concern. Under normal conditions, a user should not be exposed to batteries' active materials. Still, these methodologies indicate that somewhere along the life cycle of the product, likely in the production of disposal stages, someone may be exposed to these hazards.

A limitation of all methodologies presented here is the identification of hazards for each material. We found discrepancies between the hazards reported by the UBA and those found in the ECHA webpage. Even within the latter, different materials suppliers will report similar hazards with different intensities. Presenting these discrepancies, as we do with the HTL, or allowing for the largest hazard, as we do with THP, may be valid options. Nevertheless we think more robust alternatives can be devised. Our next step is to combine both the hazard traffic light method and THP with probabilistic indicators. Our aim is to create a qualitative and easy-to-interpret method for the comparison of different materials in the spirit of CATE methodologies, such as USEtox and USES LCA.

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