

Potential Environmental Impacts of Light-Emitting Diodes (LEDs): Metallic Resources, Toxicity, and Hazardous Waste Classification

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Light-emitting diodes (LEDs) are advertised as environmentally friendly because they are energy efficient and mercury-free. This study aimed to determine if LEDs engender other forms of environmental and human health impacts, and to characterize variation across different LEDs based on color and intensity. The objectives are as follows: (i) to use standardized leachability tests to examine whether LEDs are to be categorized as hazardous waste under existing United States federal and California state regulations; and (ii) to use material life cycle impact and hazard assessment methods to evaluate resource depletion and toxicity potentials of LEDs based on their metallic constituents. According to federal standards, LEDs are not hazardous except for low-intensity red LEDs, which leached Pb at levels exceeding regulatory limits (186 mg/L; regulatory limit: 5). However, according to California regulations, excessive levels of copper (up to 3892 mg/kg; limit: 2500), Pb (up to 8103 mg/kg; limit: 1000), nickel (up to 4797 mg/kg; limit: 2000), or silver (up to 721 mg/kg; limit: 500) render all except low-intensity yellow LEDs hazardous. The environmental burden associated with resource depletion potentials derives primarily from gold and silver, whereas the burden from toxicity potentials is associated primarily with arsenic, copper, nickel, lead, iron, and silver. Establishing benchmark levels of these substances can help manufacturers implement design for environment through informed materials substitution, can motivate recyclers and waste management teams to recognize resource value and occupational hazards, and can inform policymakers who establish waste management policies for LEDs.

Introduction

Light-emitting diodes (LEDs) are emerging as widely distributed sources of lighting because they are advertised as having better energy efficiency than other lighting sources, and as being more environmentally friendly because they do not contain mercury (1–4). It is not clear, however, whether

the material content of the LEDs, which generally include group III–V semiconductors, presents its own set of potential environmental impacts, especially when disposed of at end-of-life.

In the last 10 years, the market for LEDs has increased dramatically with an expanded diversity in applications including: colored light applications such as traffic signals, pedestrian crossings, exit signs, and decorative holiday lights; indoor white-light applications such as task lighting; and outdoor white-lighting such as path lighting (5). In addition to these applications, which use small “indicator” or “pin-type” LEDs, full-size bulbs made with high brightness LEDs (also referred to as high power or high intensity LEDs) are becoming popular for direct substitution of conventional bulbs for room lighting (4–6). The focus of the current study is on the small indicator type LEDs, because they represent a rapidly growing market of products that are widely distributed, making them difficult to manage at end-of-life. Furthermore, because of their small size, relative simplicity, and ubiquitous use, they provide an appropriate benchmark for quantifying the potential environmental impact of LEDs.

The rapid growth in the LED industry implies that, ultimately, LEDs will contribute to the solid waste stream, and could impact resource availability, human health, and ecosystems in much the same way as generic electronic waste (e-waste) from computers and cell phones has generated concern in recent years (7). To put this in context, the U.S. imports over 120 million sets of holiday lights each year, representing ~12 billion individual bulbs, most of which now consist of LEDs (5); whereas, the U.S. cellular phone sales volume in recent years has been ~200 million units annually (8). It should be noted here that cell phones weigh on the order of ~100–200 g, whereas bulbs for holiday lighting weigh far less (~10–50 g), and that these products, as well as other LED-based lighting and other electronic devices, are complex systems, within which the materials of concern may constitute just a small fraction of the product’s total weight.

Since the principle of LED lighting derives from the application of group III–V semiconductors (9), LED chips can contain arsenic, gallium, indium, and/or antimony (4, 9). These substances have the potential to cause human health and ecological toxicity effects (10). Furthermore, an LED chip is assembled into a usable pin-type device through the application of leads, wires, solders, glues, and adhesives, as well as heat sinks for thermal dissipation management (4, 9). These ancillary technologies contain additional metals such as copper, gold, nickel, and lead (Pb). Although organic compounds such as brominated flame retardants might also be used in the transparent plastic housing of LEDs and can be harmful to the environment, this study is focused on the metals in the LEDs.

Thus, the objectives of this study are as follows: (i) to use standardized leachability tests to examine whether pin-type LEDs are to be categorized as hazardous waste under existing United States federal (Toxicity Characteristics Leaching Procedure; TCLP) and California (Total Threshold Limiting Concentrations; TTCL) regulations; and (ii) to use material life cycle impact and hazard assessment methods to evaluate resource depletion and toxicity potentials of pin-type LEDs based on their metallic constituents. Satisfaction of these objectives should provide guidance to manufacturers wanting to implement design for environment (DfE), and to recyclers and waste management teams wanting to maximize resource recovery while minimizing occupational hazards due to toxic exposures.

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TABLE 1. Select LED Samples

sample name (color/intensity)	red/low	red/high	yellow/low	yellow/high	green/low	green/high	blue/low	blue/high	white
LED color	red	red	yellow	yellow	green	green	blue	blue	white
semiconductor material	GaAsP	InGaAlP	GaAsP	InGaAlP	GaP	GaN	GaN	GaN	InGaN
peak emission wavelength (nm)	625	644	590	591	565	525	430	475	n/a
full viewing angle (degrees)	30	8	30	6	30	20	10	20	20
power dissipation (mW)	105	125	105	125	105	120	140	120	100
luminous intensity (mcd)	150	6000	50	9750	50	5000	400	900	10000

Materials and Methods

Samples of LEDs Used for this Study. Nine 5-mm (T1–3/4) pin-type LEDs, purchased from Purdy Electronics Corporation (Sunnyvale, CA) and weighing on average ~300 mg each, were selected for this study (see Table 1, as well as Table S-1 and Figure S-1 in the Supporting Information (SI), for details). The LEDs represent various colors and luminous intensities. The LEDs include various III–V semiconductor materials that emit light with a specific range of wavelengths. Details on these materials, emission wavelengths, as well as other attributes, including full viewing angle and power dissipation, are provided in Table 1.

The color LEDs are further categorized for the purpose of comparison in this study as having either low or high intensities, relative to each other. The low-intensity color LEDs (with luminous intensities ranging from 50 to 400 mcd) are suitable for single-LED indicator applications (9); the high-intensity color LEDs (with luminous intensities ranging from 900 to 9000 mcd) can be used for lighting applications such as outdoor message signboards (11). The white LED has a luminous intensity of 10 000 mcd and is suitable for use in liquid-crystal display (LCD) backlighting and automotive applications (11).

Twenty metals, identified in the next section, were analyzed in each LED. The transparent plastic housing was outside the scope of this study, but would be interesting future work due to the potential end-of-life implications of managing polymeric materials (12). We used new LEDs for this work with the understanding that material content does not deteriorate with use because LED “burn-out” is caused primarily by thermo-mechanical stresses, which do not affect material composition (4).

Determination of Hazardous Waste Potential and Metallic Content of LEDs. To evaluate hazardous waste potential, two toxicity characterization methods were used: (i) the U.S. Environmental Protection Agency’s TCLP (13), which is designed to estimate the concentration of substances that would leach in landfill facilities, as defined by federal regulations; and (ii) the California Department of Toxic Substances Control’s TTLC method (14), which is used to determine whether defunct products would be classified as hazardous waste under State of California regulations (see Table S-2 of the SI for details). The TTLC also provides data on the metallic constituent, which we use here to also evaluate resource depletion and toxicity potentials. To determine the concentration of each metal detected in the TCLP and TTLC procedures, we used U.S. EPA method 6010B (15) for barium, chromium, copper, nickel, silver, and zinc; and U.S. EPA method 6020A (16) for aluminum, antimony, arsenic, cerium, gadolinium, gallium, gold, indium, iron, lead (Pb), mercury, phosphorus, tungsten, and yttrium. The TCLP and TTLC results were compared to the respective threshold limits to identify hazardous waste potential.

Evaluation of Resource Depletion and Toxicity Potentials for LEDs. Evaluations of resource depletion and toxicity potentials were based on LED metallic content and the respective weighting factors derived from established life cycle impact-based and hazard-based assessment method-

ologies. These methodologies, summarized in Table 2 and described briefly below, represent a diverse set of well-recognized methods, each formulated on the basis of unique assumptions, models, and data sets. Although each of these methods also corresponds to their own individual set of strengths, weaknesses, and inevitable data gaps, when used collectively, such as in the present study, the results can be used to provide various stakeholders with a more robust collection of information for decision-making (17).

The formula used to calculate the resource depletion or toxicity potential associated with each metal is:

$$P_i = C_i \cdot W \cdot WF_i \quad (1)$$

where P_i is a potential (i.e., life cycle impact-based resource depletion potential; hazard-based occupational toxicity potential; hazard-based Toxic Potential Indicator (TPI); and life cycle impact-based toxicity potentials for cancer, non-cancer, and ecotoxicity, as listed in Table 2) from metal i ; C_i is the content of metal i in the LED (kg/kg); W is the weight of the LED (kg); and WF_i is the weighting factor for the potential for metal i .

For life cycle impact-based resource depletion potential, the weighting factors are the characterization factors for abiotic resource depletion potential derived from the CML 2001 (18) and EPS 2000 (19) methodologies. For hazard-based occupational toxicity potential, the weighting factors are derived as the inverse of the exposure limits, i.e., Threshold Limit Value (TLV)–Time Weighted Average (TWA) (20), Permissible Exposure Limit (PEL)–TWA (20), and Reference Exposure Limit (REL)–TWA (20). For the hazard-based Toxic Potential Indicator (TPI) (21, 22), the weighting factors are calculated from R-phrase (hazardous substance declarations such as flammability, reactivity, and toxicity), Water Hazard Class, Maximum Admissible Concentration (MAK), European Union carcinogenicity, and Technical Guidance Concentration (TRC) data, by using the TPI calculator (21).

For life cycle impact-based toxicity potential, the weighting factors are the characterization factors for cancer, noncancer, and ecotoxicity potentials, respectively, derived from the Tool for the Reduction and Assessment of Chemicals and other environmental Impacts (TRACI) (23). These evaluations are based on the metal content in the LEDs, and do not take into account the materials used in the manufacturing processes or the transport pathways for the metals in landfill and incinerator facilities due to the lack of data on distribution ratio for metals into flue gas and ashes, as noted in the work by Lim and Schoenung (10). Therefore, the resource depletion and toxicity potentials represent the best and worst case scenarios, respectively. The total of a given potential for a select LED was calculated by summing the respective potentials of all the metals.

Results and Discussion

Metallic Contents from LEDs. The results of the TTLC assessment (Table 3) indicate that the LEDs included in this study contain high levels of iron (range: 256 499–398 630 mg/kg), copper (32–3892 mg/kg) and nickel (1541–4797 mg/

TABLE 2. Methods Used in This Study to Assess Resource Depletion and Toxicity Potentials

impact category	assessment method			
	scheme	characteristics for weighting factor	unit	developer
resource depletion potential	CML 2001 (18)	ratio between quantity of resource extracted and reserve	kg antimony-eq ^a	University of Leiden, Netherlands
toxicity potential	EPS 2000 (19)	resource price from market scenario	Environmental Load Unit (ELU)	Chalmers University of Technology
	Threshold Limit Value (TLV)-Time Weighted Average (TWA) (20)	relative hazard for occupational exposure limit: inverse of the limit	m ³	American Conference of Governmental Industrial Hygienists (ACGIH)
	Permissible Exposure Limit (PEL)-TWA (20)	relative hazard for occupational exposure limit: inverse of the limit	m ³	U.S. Occupational Safety and Health Administration (OSHA)
	Reference Exposure Limit (REL)-TWA (20)	relative hazard for occupational exposure limit: inverse of the limit	m ³	U.S. National Institute for Occupational Safety and Health (NIOSH)
	Toxic Potential Indicator (TPI) (21)	-R-phrase (hazardous substance declaration)—water hazard class—maximum admissible concentration (MAK), EU carcinogenicity, technical guidance concentration (TRC)	TPI	Fraunhofer IZM, Germany
life cycle impact-based	Tool for the Reduction and Assessment of Chemical and other environmental Impacts (TRACI) (23)	toxicological properties such as fate, exposure, and effect for cancer, noncancer, and ecotoxicity potentials	cancer: kg benzene-eq ^a —noncancer: kg toluene-eq ^a —ecotoxicity: kg 2,4-dichlorophenoxyacetic acid-eq ^a	U.S. Environmental Protection Agency (EPA)

^a "eq": equivalent.

TABLE 3. Results of Total Threshold Limit Concentrations (TTLC) tests^{a,b,c}

substance	TTLC threshold	LED (color/intensity)								
		red/low	red/high	yellow/low	yellow/high	green/low	green/high	blue/low	blue/high	white
aluminum	N/A	97.0	158.0	104.0	156.0	79.6	156.0	153.0	73.4	84.5
antimony	500	15.4	2.0	2.8	1.9	3.6	2.5	1.3	1.5	25.9
arsenic	500	11.8	111.0	8.0	84.6	7.8	15.2	5.7	5.4	ND
barium	10000	ND	ND	ND	ND	ND	ND	ND	ND	ND
cerium	N/A	ND	ND	ND	ND	ND	ND	ND	ND	ND
chromium	500(VI);2500(III)	138.0	28.6	32.7	27.9	84.1	49.3	50.9	30.3	65.9
copper	2500	87.0	3818.0	956.0	2948.0	1697.0	3702.0	3892.0	2153.0	31.8
gadolinium	N/A	ND	ND	ND	ND	ND	ND	ND	ND	ND
gallium	N/A	135.6	95.0	63.8	79.1	75.6	3.1	2.1	1.5	3.8
gold	N/A	39.8	45.8	30.5	30.1	40.2	176.3	32.5	118.6	115.9
indium	N/A	3.4	1.7	ND	ND	2.5	ND	ND	ND	ND
iron	N/A	285558	363890	300905	398630	310720	395652	339234	256499	311303
lead	1000	8103.0	8.9	7.7	ND	5.0	ND	ND	ND	ND
mercury	20	ND	ND	ND	ND	ND	ND	ND	ND	ND
nickel	2000	4797.0	2054.0	1541.0	2192.0	2442.0	2930.0	1564.0	1741.0	4083.0
phosphorus	N/A	114.2	ND	58.4	ND	78.5	91.8	79.1	84.3	110.8
silver	500	430.0	409.0	248.0	336.0	270.0	306.0	418.0	721.0	520.0
tungsten	N/A	ND	ND	ND	ND	ND	ND	ND	ND	ND
yttrium	N/A	ND	ND	ND	ND	ND	ND	ND	ND	ND
zinc	5000	48.2	66.2	36.5	63.6	41.8	62.5	42.6	36.7	49.2

^a The values in bold indicate that the TTLC results exceed the regulatory limit. The unit of measurement is mg/kg. ^b N/A: Not Applicable. ^c ND: Not Detected.

TABLE 4. Results of Toxicity Characteristics Leaching Procedure (TCLP) Tests^{a,b,c,d}

substance	TCLP threshold	LED (color/intensity)								
		red/low	red/high	yellow/low	yellow/high	green/low	green/high	blue/low	blue/high	white
iron	N/A	332.5	178.3	206.0	163.5	211.8	161.8	178.5	130.8	202.3
lead	5.0	186	ND	ND	ND	ND	ND	ND	ND	ND

^a The value in bold indicates that the TCLP result exceeds the regulatory limit. The unit of measurement is mg/L. ^b The metals that were not detected by TCLP are not provided here: aluminum, antimony, arsenic, barium, cerium, chromium, copper, gadolinium, gallium, gold, indium, mercury, nickel, phosphorus, silver, tungsten, yttrium, and zinc. The complete list is provided in Table S-4 in the SI. ^c N/A: Not Applicable. ^d ND: Not Detected.

kg). In comparison, the levels for gold (30–176 mg/kg), silver (248–721 mg/kg), and group III–V semiconductor materials (not detectable concentration to 136 mg/kg) were much lower. Barium, cerium, gadolinium, mercury, tungsten, and yttrium were not detected in any of the LEDs. The lead (Pb) content of low-intensity red LED was 8103 mg/kg, which is higher than the levels determined for the other LEDs by at least 3 orders of magnitude. The combined weight of these metals corresponds to approximately one-third the total LED weight, regardless of color or intensity (Tables S-1 and S-3 and Figure S-2 of the SI); the remaining weight is derived from the plastic housing.

Hazardous Waste Potential. Most LEDs would be classified as hazardous waste under California regulations, but not under U.S. EPA federal regulations. Results of TCLP analysis show that the only regulatory limit that was exceeded is for lead (Pb) in the low-intensity red LED (Table 4 and Table S-4 of the SI). In contrast, TTLC results (Table 3) show that all LEDs except the low-intensity yellow LED exceed California’s regulatory limits for copper, lead (Pb), nickel, and/or silver. It is noteworthy that several metals that we detected have no established regulatory threshold limits at the federal or state level. These metals are either considered nontoxic, or without sufficient information to regulate them appropriately.

These results imply that adoption of DfE strategies will necessitate reductions in copper, lead (Pb), nickel, and silver content so that waste LEDs do not exceed the threshold limits of these metals according to established hazardous waste

regulations. As LEDs gain in usage for ambient lighting and in flat panel displays, it is important to reconsider their perception as “environmentally-friendly” and to encourage desirable changes in their toxic constituents through product design that includes safer alternatives.

The discrepancy between federal and state regulations governing hazardous waste classification warrants attention to avoid confusion in product classification and consumer practices that will be needed to support policies on recycling and waste disposal. In addition, it is important to develop seamless regulatory policies across international boundaries. For example, it is likely that the absence of lead (Pb) in most of the LEDs tested is due in part to the European Union’s Restriction on Certain Hazardous Substances (24) and/or the California’s Electronic Waste Recycling Act (CEWRA) (25), which limit the use of lead (Pb) in electrical and electronic equipment. No similar federal laws have been enacted in the United States.

Resource Depletion Potentials. The resource depletion potentials measured in units of kg of antimony-equivalents (Sb-equiv) and Environmental Load Units (ELUs) for the fourteen metals detected in the LEDs are depicted in Figure 1a. The substances with considerable impact on resource depletion are gold and silver (~10⁻⁶ kg Sb equiv or ~10⁻² ELU), even though they are present in small amounts in the LEDs (<0.02 wt % for gold, <0.07 wt % for silver). Copper, nickel, iron, and lead (Pb) exhibit measurable, but lower, resource depletion potentials (~10⁻⁹ kg Sb equiv or ~10⁻⁴ ELU). The resource depletion potentials for the group III–V

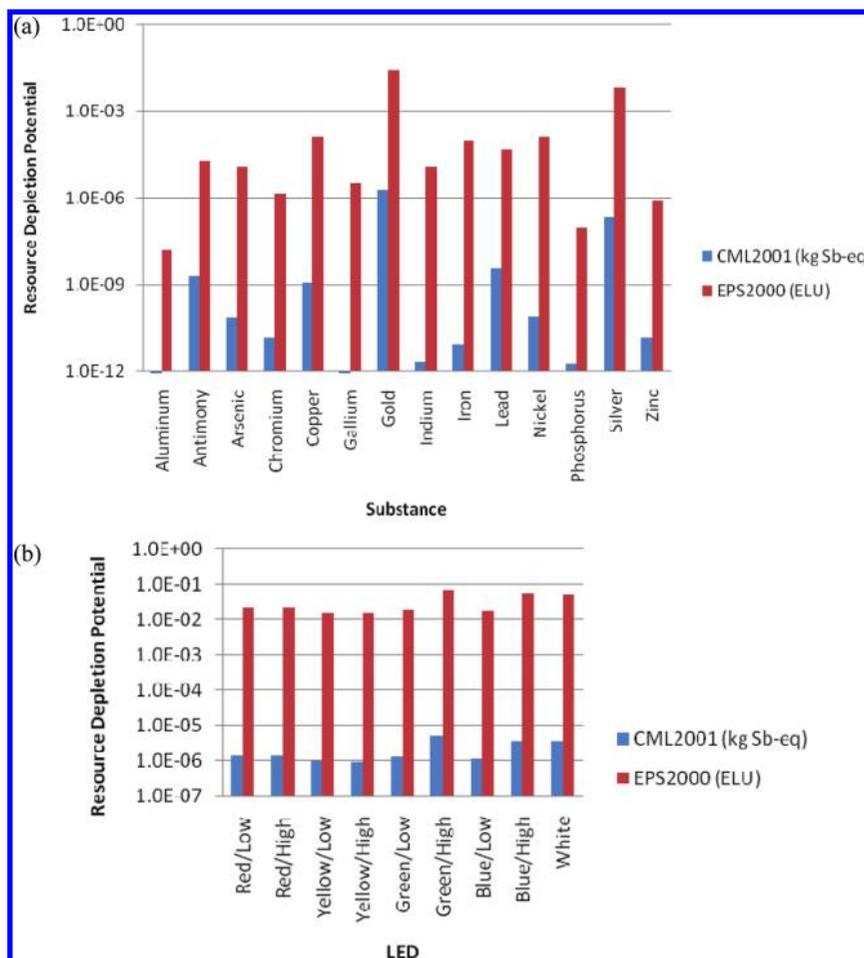


FIGURE 1. Resource depletion potentials derived on the basis of the CML 2001 and EPS 2000 methods: (a) for each metal detected in the LEDs, and (b) aggregated values for each LED. Quantitative values for the potentials are provided in Tables S-5 and S-6 in the SI.

semiconductor materials (antimony, arsenic, gallium, and indium) are approximately one more order of magnitude lower. The total resource depletion potentials for the nine LEDs show limited variability, within an order of magnitude with both evaluation methods (Figure 1b).

If the metal content of LEDs remains unchanged and the demand for their use continues at the current pace, then we should expect considerable impacts on the distribution of gold and silver resources (26). Gold, which has low electrical and thermal resistivity and thus minimizes the possibility of LED damage caused by poor thermal management, is used as the conductive metallic wires to connect the pin-type electrode to the LED chip (4). Silver is used as a coating material to effectively reflect the light from the LED chip (4). Although not quantitatively evaluated in the current study, implications of the expanding market beyond pin-type LEDs to surface mount LEDs can be qualitatively considered here, knowing that for surface mount LEDs, as currently designed, more gold and silver are needed than in the traditional pin-type LEDs (4). Gold is then used, for instance, as the finishing on the heat sink, as the stud bumps used for lateral flip chip LEDs, and in the solder layer (80/20 gold–tin by weight). LEDs with higher luminous intensities also require more gold wires and/or larger cross-sectional diameters. Silver is then used, for instance, as the coating and finishing on the heat sink, and in epoxy–silver–based adhesives and glue. Therefore, ancillary LED technology, more so than the LED chip itself, should be redesigned to reduce the use of gold and silver, in the context of dFe. In addition, because of the valuable gold and silver content in existing LEDs, recycling technologies need to be rapidly developed and implemented.

Toxicity Potentials. We investigated the contributions of the toxicity characteristics for each of the fourteen metals to the overall toxicity potential of LEDs. The results show that copper, iron, lead (Pb), nickel, and silver contribute most to the hazard potential, since each represents at least 10% of the combined hazard potential from all fourteen metals for at least one assessment method (Figure 2a). It should be noted that the toxicity characteristics for iron oxide were used here because data do not exist for metallic iron. The group III–V semiconductor materials (antimony, arsenic, gallium, and indium) exhibit relatively low contributions to the hazard potentials. Although for 6 of the 14 metals, at least one assessment method could not be used because of data gaps, by utilizing a collection of assessment methods, each metal is accounted for by at least one method. Although the TPI methodology accounts for a wider range of hazards (e.g., ecological) than the other methods based on occupational exposure limits, there is consistency in the outcome of the different methods in terms of metals that are identified as contributing most to the toxicity hazard potentials. When we examined differences in toxicity hazard potential among the different LEDs (Figure 2b), we found that low-intensity red LEDs exhibit the highest level, due to the high content of lead (Pb) and that high-intensity LEDs generally exhibit higher toxicity hazard levels than their low-intensity equivalents, due to their higher concentrations of copper, iron, and nickel.

We also used a life-cycle impact method (TRACI) to evaluate the relative contribution of each metal to the toxicity potentials. The results implicate arsenic and lead (Pb) as the highest contributors to cancer potential; lead (Pb) and copper

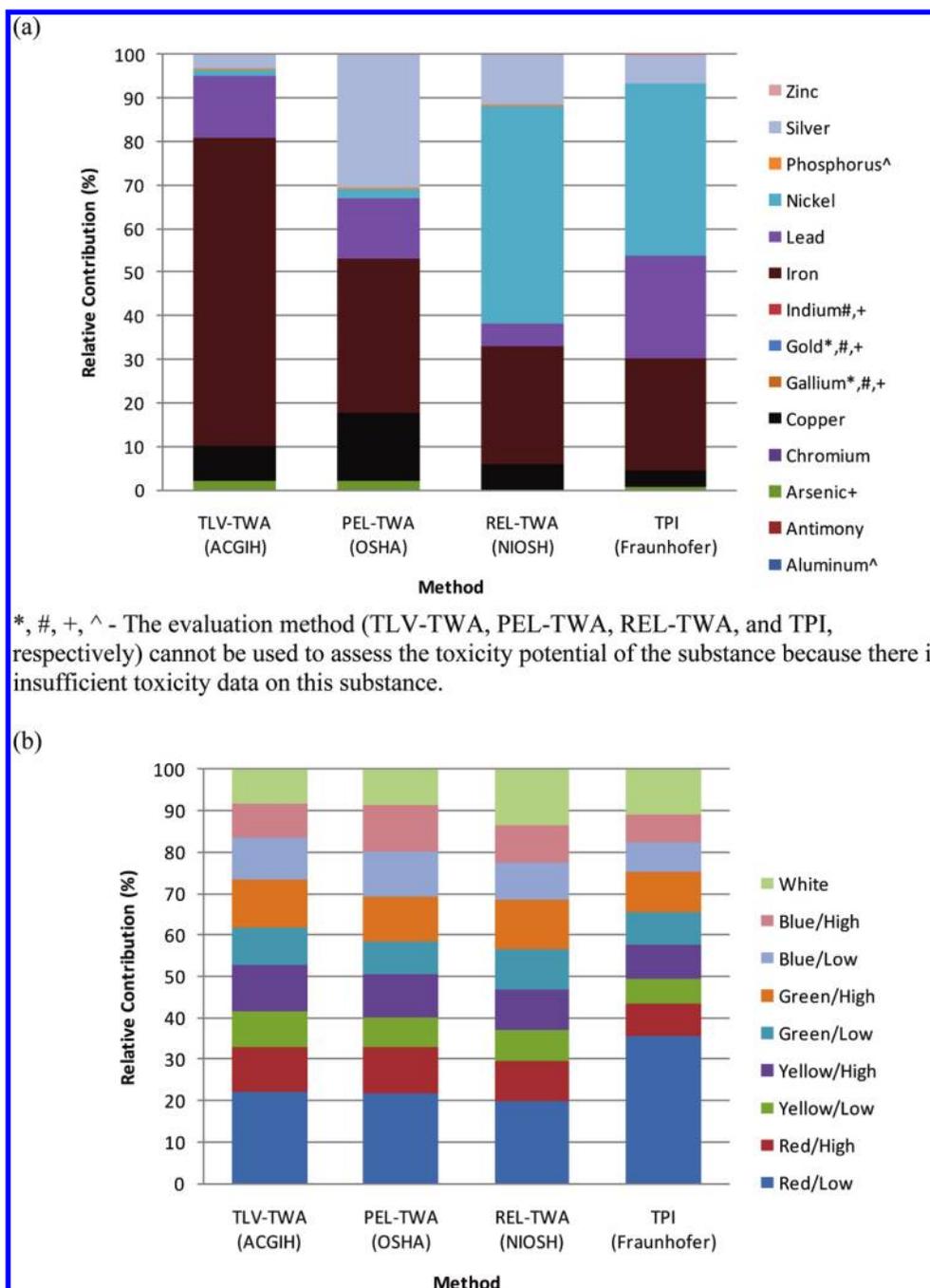


FIGURE 2. Hazard-based toxicity potentials derived on the basis of the TLV-TWA, PEL-TWA, REL-TWA, and TPI methods: (a) relative contribution of each metal detected in the LEDs to the total potential of all of the metals based on average metal contents of the LEDs, and (b) relative contribution of each LED to the total potential of all of the LEDs. Quantitative values for the potentials are provided in Tables S-7, S-8, S-9, and S-10 in the SI.

for noncancer potential; and copper and nickel for ecotoxicity potential (Figure 3a). Arsenic is the only substance among the group III–V semiconductor materials to exhibit considerable cancer potential. We could not use TRACI to assess the contributions of four metals (gallium, gold, indium, and iron) because they are not included in the TRACI database.

Comparing the TRACI results for the different LEDs (Figure 3b), we find the low-intensity red LEDs exhibit significant cancer and noncancer potentials due to the high content of arsenic and lead (Pb). For the yellow LEDs, the high-intensity devices exhibit higher toxicity potentials than the low-intensity ones due to the higher content of arsenic and copper. With the exception of the low-intensity yellow LEDs and the white LEDs, which have relatively low ecotoxicity potentials, all of the other LEDs exhibit consistent levels of ecotoxicity

potentials due to the copper and/or nickel content. Overall, the white LEDs exhibit relatively low toxicity potentials because they contain less copper and do not contain arsenic or lead (Pb).

The effectiveness of the DfE concept depends on how closely we can pinpoint specific materials in products that render them hazardous for environmental quality and human health. Through this research, we have demonstrated that the content of copper, nickel, lead (Pb), and silver contribute to the hazardous waste potential for pin-type LEDs; whereas the gold and silver contribute the most to resource depletion potential; copper, iron, nickel, lead (Pb) and silver all contribute to hazard potential; and arsenic, lead (Pb), copper and nickel are of greatest concern for human and ecological health. It is interesting to note that other than arsenic, the

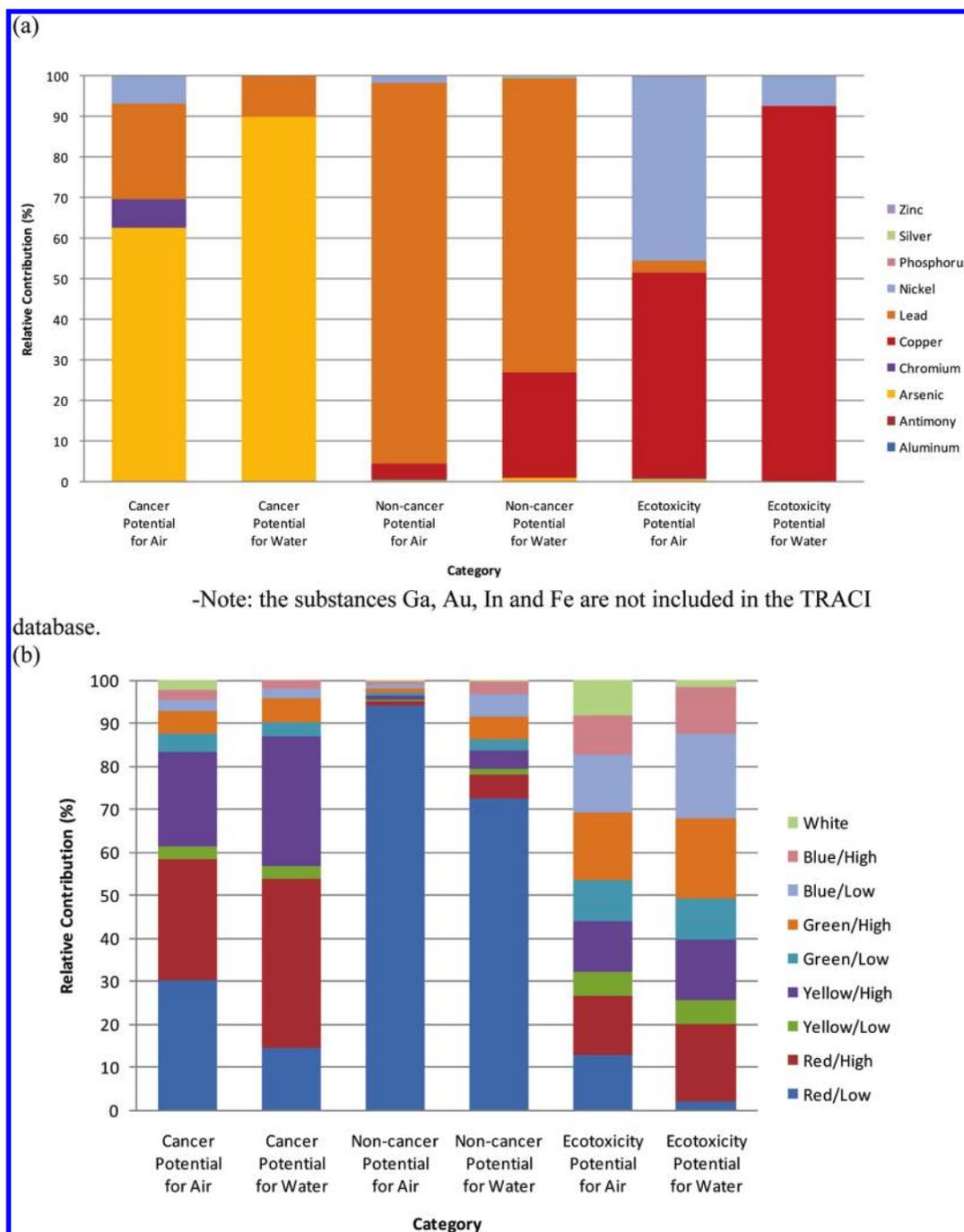


FIGURE 3. Life cycle impact-based toxicity potentials determined on the basis of the TRACI method: (a) relative contribution of each metal detected in the LEDs to the total potential of all of the metals based on average metal contents of the LEDs, except Ga, Au, In, and Fe, which are not included in the TRACI database; and (b) relative contribution of each LED to the total potential of all of the LEDs. Quantitative values for the potentials are provided in Table S-11 in the SI.

group III–V semiconductor materials are not of concern. Among the LEDs tested, white LEDs seem to be the safest for the environment because of the absence of toxic substances such as arsenic and lead (Pb). To the extent that these results can be used to guide the development of manufacturing and product design practices, attempts should be made to reduce the content of these targeted substances, provided alternatives are first evaluated through equally rigorous assessment, in an effort to avoid undesirable substitutions before products are marketed in large volumes to consumers. Further investigation of additional types of LEDs (such as surface mount) and actual LED bulbs is also necessary to provide a robust assessment of the potential environmental impact of these emergent technologies. The results of this study further indicate that despite a wide range

of well-established assessment methods, decision-making is ultimately hampered by a lack of basic toxicity data for metals in general and for the group III–V semiconductor materials in particular.

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Supporting Information Available

Details on the materials, methods, and quantitative results. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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