

Expert statement on LCA of Cd vs. non-Cd options for colour conversion in displays and lighting systems

QD Vision, Inc./Linnunmaa Ltd

Headline Expert statement on LCA of Cd vs. non-Cd options for colour conversion in displays and lighting systems	Date 20.12.2012	Project number 11545
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Pages 20 p.	Distribution Customer 1 pc Linnunmaa Oy 1 pc	

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1 GOAL DEFINITION

This is an expert statement intended as an initial step toward a life-cycle assessment (LCA). Its goal is to compare the life-cycle of light-emitting diodes (LEDs) which contain cadmium-based colour-converting material (quantum dot (QD) downconversion material) for use in solid-state illumination and display systems, a new technology intended to be introduced on the market in the European Union, with the most relevant corresponding technologies in current use in the EU. The assessment is based on available information and literature and concentrates on potential toxic emissions during use and end-of-life waste management of QD components (cadmium) and the corresponding current technologies (mercury and rare earth metals) as well as energy consumption during the use life of illumination and display systems in order to show the differences in environmental and health safety point of view.

This statement is provided in support of an application by QD Vision, Inc., in December, 2012 for the renewal of Exemption 39 under Directive 2011/65/EU (RoHS II – Restriction of Hazardous Substances), which restricts the use of certain hazardous substances including cadmium in electric and electronic equipment.

2 BACKGROUND

2.1 The product

The product under consideration in this assessment is the Cd-containing color downconversion component. The cadmium-containing quantum dots are nanoparticle structures of a cadmium selenide (CdSe) core within a zinc sulfide (ZnS) shell which are embedded in an acrylate polymer matrix as a nanocomposite sealed in glass. The resulting glass-covered component can be used with LED-based lighting systems and display backlighting. Corresponding products have been on the market in the US since 2010 but have not yet been placed on the market in the EU.

2.2 The toxicology and general exposure to cadmium and some rare earth metals (REMs) used in color downconversion

2.2.1 Cadmium

Emissions and atmospheric deposition

Cadmium is a non-essential metal and as an element it is persistent in the environment. It is released to the environment from a variety of natural and anthropogenic sources. Natural sources include mainly volcanic activity, weathering of rocks and forest fires, and the primary anthropogenic sources are metal production, fossil fuel combustion, open burning or incineration of wastes and cement production (UNEP, 2010). Also use of cadmium containing phosphate minerals and fertilizer, mobilization of cadmium from previously deposited soils, sediments, landfills and mine dumps are of importance.

Cadmium is mainly as a by-product of zinc, lead and copper production. Annual world production is about 20 000 tonnes, and it has remained rather constant since 1990 (UNEP, 2010). Recycled cadmium accounts for about 18% of total global supply. Based on recent estimates the total emissions of cadmium from natural sources is 15 000 – 88 000 tonnes per year. There is some uncertainty in the estimates, but the natural emissions are likely to be 5 – 30 times higher than anthropogenic emissions. However, industrial emissions have been important in the long range transportation of cadmium.

Global anthropogenic cadmium emissions were estimated at 2 983 tonnes in the mid-1990's, and the emissions were estimated to have decreased by about 50% until 2003 in developed countries. According to the WebDab database of the Co-operative programme for monitoring and evaluation of long range transmission of air pollutants in Europe (<http://www.ceip.at/webdab-emission-database/>) the officially reported cadmium emission in the was EU 258 tonnes in 1990 and 103 tonnes in 2010 showing a decrease by 60% in 20 years (Fig. 1).

In accordance with decreasing emissions also environmental concentrations of cadmium show a similar decreasing trend as indicated by an European scale biomonitoring of heavy metals in mosses between 1995 and 2005 (Harmens et al., 2008). Moss analysis provides a convenient, time-integrated method for quantification of atmospheric deposition of heavy metals to terrestrial systems. Between 1990 and 2005, the average medium cadmium

concentration in mosses declined by 52% in 16 European countries (Figs. 2. and 3.). Waste incineration was the main anthropogenic source for cadmium emission in Europe in 1990, but its contribution was strongly reduced thereafter. In 2005 the main sources were “manufacturing industries and construction” (45%) and “public electricity and heat production” (21%) (Ilyin et al., 2007). Also in agricultural areas cadmium emissions from phosphate fertilizers declined strongly between 1990 and 2005. In Finland, where no single industrial cadmium emission sources could be highlighted, the decrease in cadmium concentrations in mosses were on average 67% (Harmens et al., 2008).

Sector: NATIONAL TOTAL
Country / Area: European Union

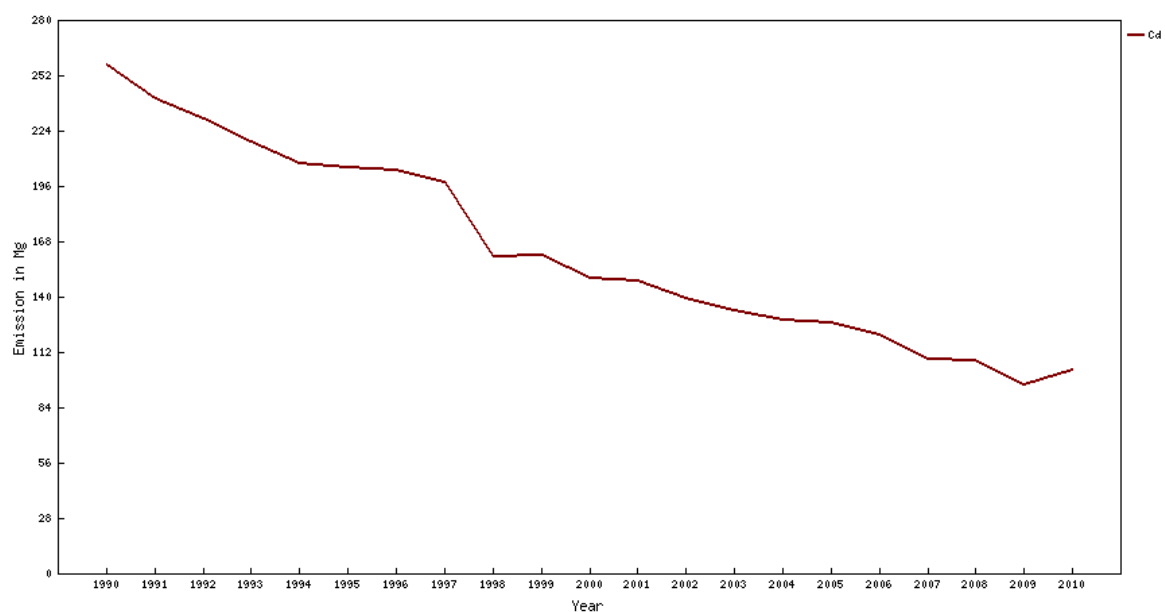


Figure 1. Cadmium emission trend in the European Union in 1990-2010. Data from the WebDab emission database of EMEP (Co-operative programme for monitoring and evaluation of long range transmission of air pollutants in Europe).

WebDab contains all emission data officially submitted to the secretariat of the Convention on Long-range Transboundary Air Pollution (LRTAP Convention) by Parties to the Convention (<http://www.ceip.at/webdab-emission-database/>).

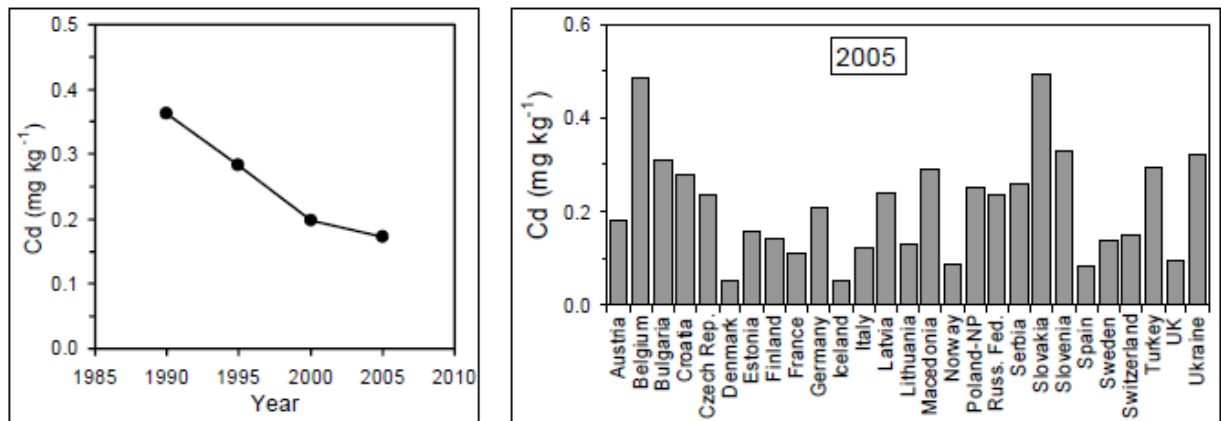


Figure 2. Average of median cadmium concentration in mosses for countries (n = 16) that reported cadmium data in all survey years (left) and median cadmium concentration in mosses per country in 2005 (right) (Harmens et al., 2008).

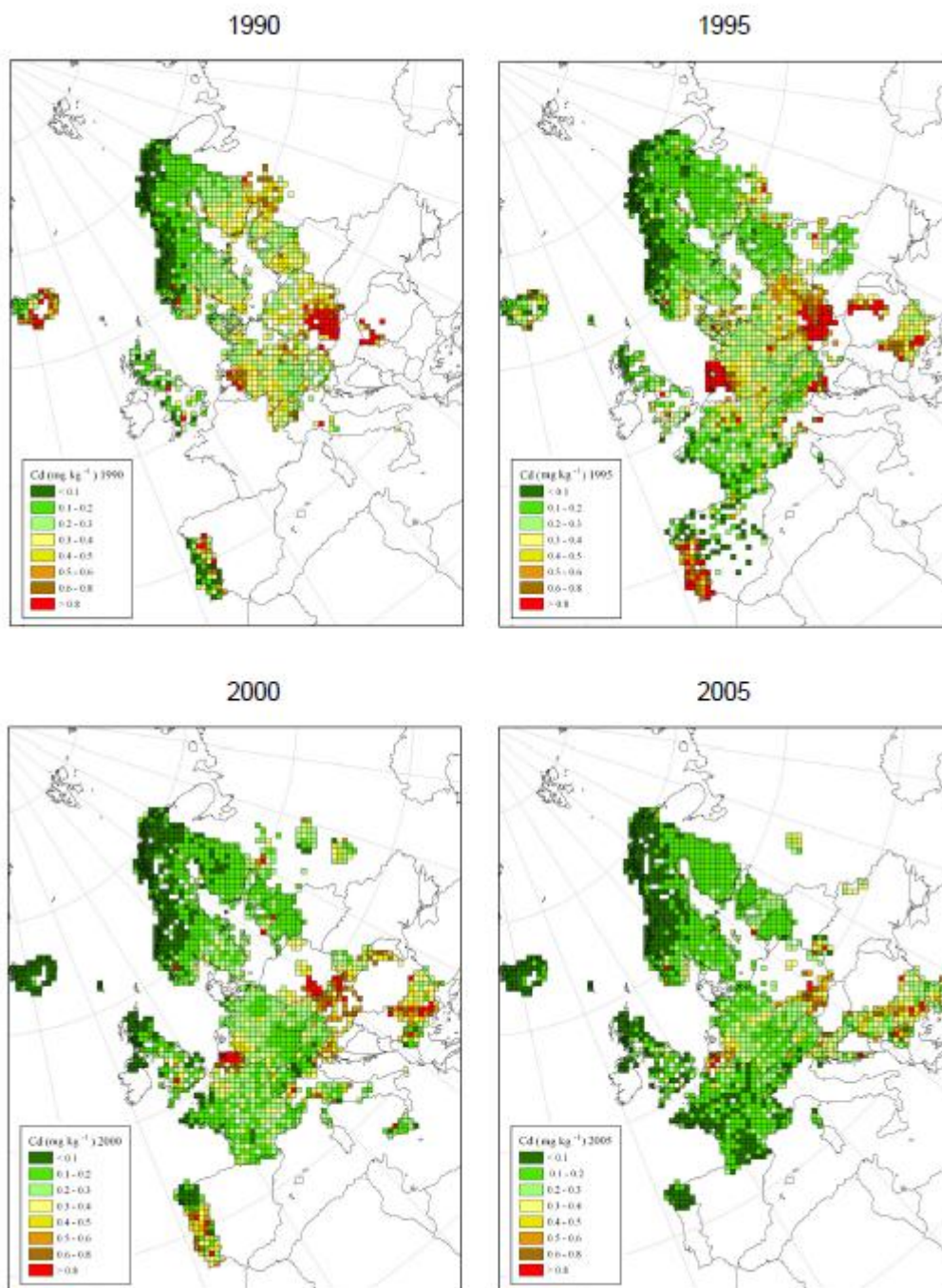


Figure 3. Mean concentration of cadmium in mosses per EMEP grid square in Europe in 1990, 1995, 2000 and 2005 (Harmens et al., 2008).

Human exposure to cadmium

Dietary exposure accounts for about 90% of the total cadmium exposure in general, non-smoking population. Most dietary cadmium comes from agricultural products, as cadmium reaches soil through atmospheric deposition and contaminated fertilizers, and plants take up the metal from soil. Less than 10% is from inhalation of low levels in ambient air and from drinking water. Tobacco is an important source of cadmium uptake in smokers and may contribute 50% of total intake. It may also affect non-smokers through passive exposure to second hand smoke.

Oral bioavailability of cadmium is only 3-5%, but as much as 30-64% of inhaled cadmium is taken up. After absorption cadmium accumulates efficiently in kidneys and liver, and the elimination half-life is as long as 10-30 years (EFSA, 2012). Kidney is the target organ of cadmium in humans and kidney damage characterized by proximal tubular damage and increased excretion of proteins in urine is the critical health effect (UNEP, 2010). Proteinuria is the most sensitive indicator of cadmium toxicity. Skeletal damage due to bone demineralization is observed at slightly higher exposure levels.

In European foods, high levels of cadmium were found in algal formulations, cocoa-based products, crustaceans, edible offal, fungi, oilseeds, seaweeds and water molluscs (EFSA, 2012). In about half of the food samples available to EFSA cadmium was not detected or levels were below the limit of quantification. Food consumed in larger quantities has the greatest impact on dietary exposure to cadmium. These include the broad food categories of grains and grain products (26.9%), vegetables and vegetable products (16.0%) and starchy roots and tubers (13.2%). In more detailed analysis potatoes (13.2%), bread and rolls (11.7%), fine bakery wares (5.1%), chocolate products (4.3%), leafy vegetables (3.9%) and water molluscs (3.2%) contributed the most to European cadmium dietary exposure.

Based on detailed individual food consumption data, middle bound average and 95th percentile lifetime cadmium dietary exposure for the European population was estimated at 2.04 and 3.66 µg/kg body weight per week, respectively. It was highest in toddlers and lowest in the elderly population group. In its re-assessment in 2009 the EFSA Panel on Contaminants in the Food Chain decreased the tolerably weekly intake (TWI) of cadmium from 5.8 to 2.5 µg/kg body weight in order to ensure a high level of protection of all consumers, including exposed and vulnerable subgroups of the population. Therefore, some subgroups may currently exceed this health-based guidance value.

2.2.2 Europium

Europium is the most reactive rare earth metal. It does not exist in the nature as a free element, but many minerals contain europium as trace element. It oxidizes readily in air and water, and resembles calcium in its reactions with water. Europium is not known to have a physiological role and it is rather non-toxic as compared with other heavy metals. LD₅₀ values for europium chloride were 550 mg/kg after intraperitoneal administration and 5000 mg/kg after oral administration (Haley et al., 1965). The same figures for europium nitrate were 320 mg/kg and >5000 mg/kg, respectively (Bruce et al., 1963). In a 28-day oral toxicity study in rats the no-observed-effect level (NOEL) of europium chloride (EuCl₃*6H₂O) was 200 mg/kg/day (Ogawa et al., 1995). Hyperkeratosis of

forestomach and eosinocyte infiltration of the stomach submucosa was observed in both sexes at 1000 mg/kg/day, suggesting a local irritation effect.

Europium dust presents a hazard for fire and explosion. No occupational exposure limit values or tolerable daily intake values are available.

2.2.3 Yttrium

Yttrium is a rare earth metal that is never found in nature as a free element. It exists almost always combined with the lanthanides in rare earth minerals. Yttrium is not known to have biological role, and exposure to yttrium compounds can cause lung disease in humans (see below). The following information is available at the OSHA document "Occupational Safety and Health Guideline for Yttrium and Compounds" (<http://www.osha.gov/SLTC/healthguidelines/yttriumandcompounds/recognition.html>):

Exposure limits and exposure routes

The current Occupational Safety and Health Administration (OSHA) permissible exposure limit (PEL) for yttrium and the compounds of yttrium (measured as yttrium) is 1 milligram per cubic meter (mg/m³) of air as an 8-hour time-weighted average (TWA) concentration [29 CFR 1910.1000, Table Z-1-A]. The National Institute for Occupational Safety and Health (NIOSH) has not issued a recommended exposure limit (REL) for yttrium and yttrium compounds. The American Conference of Governmental Industrial Hygienists (ACGIH) has assigned yttrium and its compounds a threshold limit value (TLV) of 1 mg/m³ (measured as yttrium) as a TWA for a normal 8-hour workday and a 40-hour workweek [ACGIH 1988, p. 38]. The OSHA and ACGIH limits are based on the risk of pulmonary effects associated with exposure to yttrium or its compounds.

Exposure to yttrium and yttrium compounds can occur via inhalation, ingestion, and eye or skin contact.

Summary of toxicology

Effects on Animals

In experimental animals, exposure to yttrium or a compound of yttrium causes damage to the lungs and liver. The toxicity of yttrium is low orally and high parenterally; toxicity also varies greatly with different yttrium compounds [Clayton and Clayton 1981, p. 1678]. The intraperitoneal LD₅₀s in rats is 45 mg/kg for yttrium chloride [RTECS 1989c], 362 mg/kg for yttrium nitrate [Sax and Lewis 1989, p. 3508], and 230 mg/kg for yttrium oxide [RTECS 1989d]. The lowest lethal subcutaneous dose of yttrium nitrate hexahydrate in mice is 16.6 g/kg [RTECS 1989b]. Rats injected intraperitoneally with 60 mg/kg yttrium every other day for 5 months survived and showed no accumulation of yttrium in their bones [ACGIH 1986, p. 641(86)]. A single intra-tracheal dose of 50 mg yttrium oxide produced diffuse granulomatous nodules and emphysema in rats within 8 months of exposure [Clayton and Clayton 1981, p. 1682]. Inhalation of yttrium citrate (at an unspecified concentration) caused dyspnea and pulmonary edema in rats [Proctor and Hughes 1978, p. 511]. Rats exposed to yttrium chloride by inhalation (at an unspecified concentration) developed liver edema (with portal congestion), pleural effusions, and pulmonary hyperemia [Proctor and Hughes 1978, p. 511]. Application of a 0.1 M solution of yttrium chloride to the intact eye

of a rabbit caused no detectable damage; the same application to eyes from which the corneal epithelium had been removed produced corneal opacification [Grant 1986, p. 986].

Effects on Humans

Based on effects seen in animals, exposure to yttrium or to a compound of yttrium would be expected to cause lung disease in humans. Workers exposed to an average airborne concentration of yttrium europium vanadate dust experienced mild eye, skin, and upper respiratory tract irritation; however, the authors of this study attributed these effects to the vanadium component of the dust [ACGIH 1986, p. 641(86)].

Signs and symptoms of exposure

Based on effects seen in animals, the signs and symptoms of acute exposure to yttrium or a compound of yttrium would be expected to include those associated with fibrotic lung disease, such as shortness of breath, cough, chest pain, and cyanosis in acute exposure. No signs or symptoms of chronic exposure to yttrium or to a compound of yttrium have been reported.

3 SCOPING

This assessment is based on outside-of-EU experiences and stated expectations regarding the exact or corresponding product (colour conversion component) under assessment, literature on waste electric and electronic equipment (WEEE) management in the EU and literature on life cycles of closely related EEE. The production of the glass component is in all cases expected to take place outside of the EU, and for this reason, the manufacture part of the life cycle is not considered in this assessment at this stage. The assessment is based on expected imported amounts of articles and Cd annually and amount and concentrations of Cd in the product as stated by the applicant.

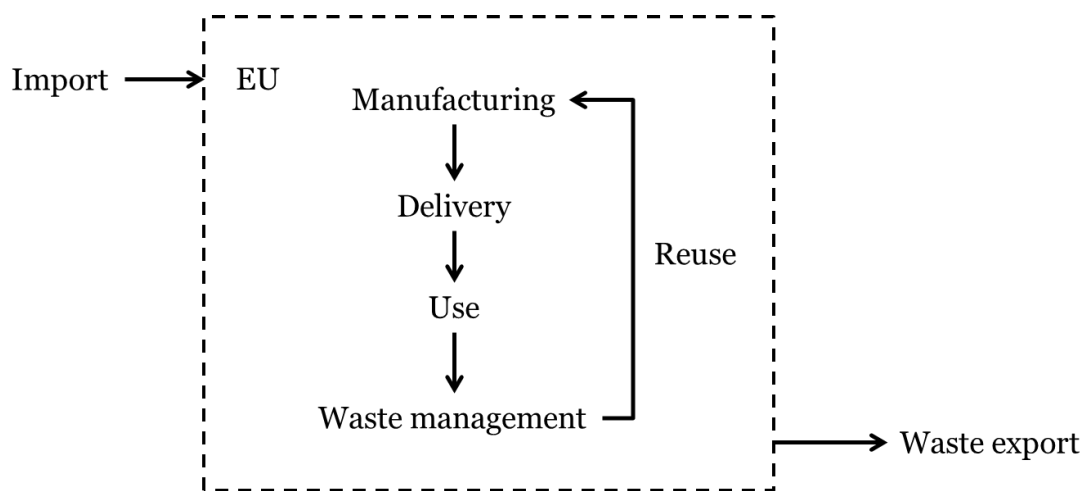


Figure 4. Life cycle of cadmium-based colour converting material in EU.

Regarding comparison technologies in current use, incandescent lamps are still in use within the EU, but as old technology of high energy consumption they are currently being phased out in the EU; therefore life-cycle comparison will mainly take place with prevalent new technology that is currently in use. For illumination systems, fluorescent lighting is considered the most relevant comparison technology. For displays (televisions, computer monitors and mobile phones), the comparison technology is liquid crystal displays (LCDs) backlit with LEDs with downconversion material based on rare earth metals (europium, yttrium, cerium).

4 DESCRIPTION OF LIFE CYCLE

4.1 Production and use

The colour-converting components that contain cadmium are expected to be produced outside of the European Union and imported as parts of sets or complete systems, in future possibly as such for assembly within EU. As the substance is bound as a solid compound (cadmium selenide; melting point > 1000 °C) within a solid matrix sealed inside a glass tube which is placed inside electric equipment, within the use life of the components (including assembly, distribution and use of complete systems, or consumer products) only accidental human or environmental exposure to Cd is likely. Even in case the glass component breaks in open air, Cd will under normal conditions remain bound in the solid polymer matrix within. However, in case the appliance is destroyed in a fire, the Cd the component contains is likely to be released into the atmosphere as a part of the generated particulate pollution.

4.2 End-of-life

The average collection rate of waste electric and electronic equipment (WEEE) within the European Union was 33 % by weight in 2008 (EEA, 2012). (It should be noted that since this percentage reflects the weight of EEE placed on the market and that of WEEE collected in the same year, which consists to an undetermined extent of EEE placed on the market years or even decades earlier, it cannot be taken as a direct probability of appropriate collection of an electric or electronic item placed on the market in 2008 at the end of its useful life; however, both collection rate and material recovery, recycling and reuse targets are currently being raised.) Of the collected WEEE, in most EU countries a high percentage (> 80 % in 21 EU countries in 2008) is recycled or reused. Of the WEEE not reported as collected, a large proportion is probably collected for informal recycling either within the EU or, after exporting, outside of it. The recycling practices involved are likely to be inappropriate regarding both human and environmental exposure to harmful substances.

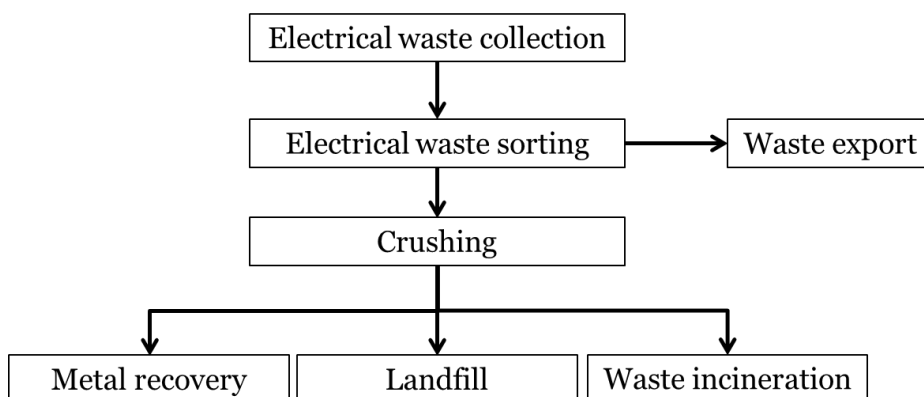


Figure 5. WEEE management in the EU.

The different waste management options and the human and/or environmental exposure involved are discussed below.

Kg per capita in 2008

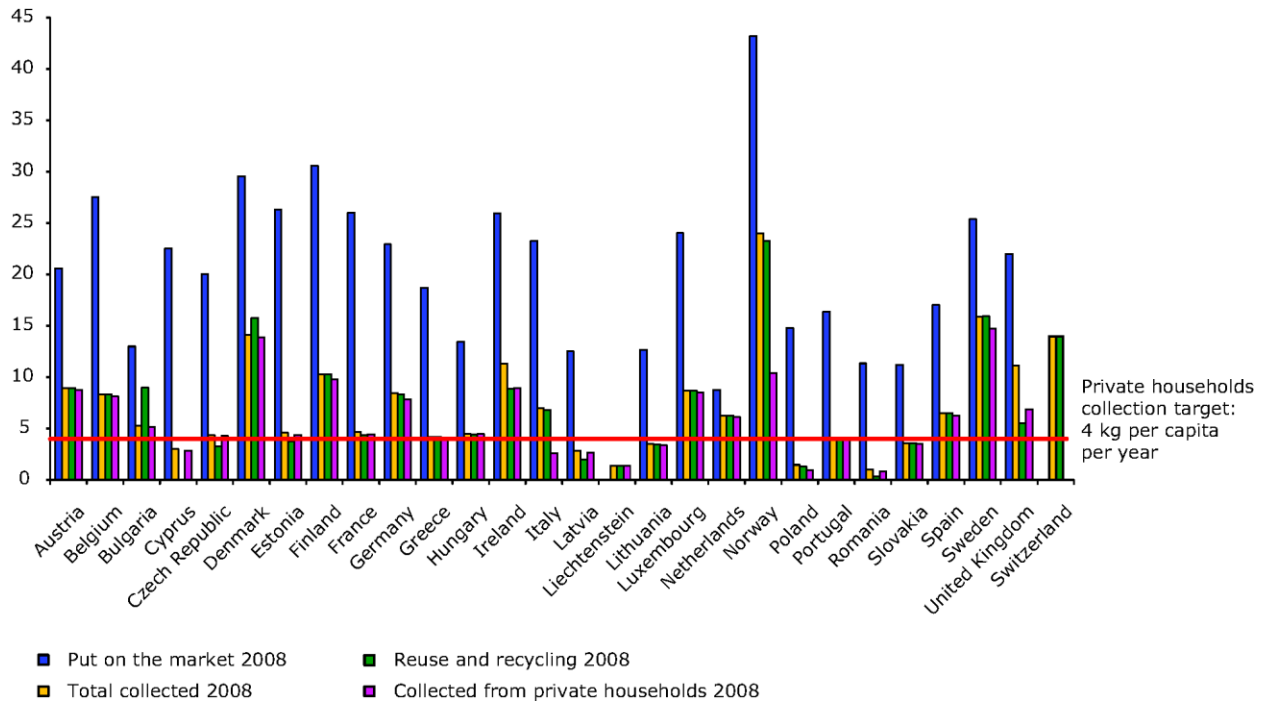


Figure 6. The collection rate of waste electric and electronic equipment within EU (EEA, 2012).

4.2.1 Take-back and recovery of isolated components

It is assumed that an appropriate take-back system through distributors will be in place for items containing the Cd-containing component in accordance with the WEEE directive (2002/96/EC). According to the manufacturer, waste management practices for this component are at this stage still under development; however, the component is designed for easy mechanical separation from the other components of the system in order to facilitate recovery and recycling.

In the best case, the materials of this component will be recycled through an end-use market for the component. A high level of cadmium extraction from the polymer matrix can be achieved by using strong acids such as nitric acid (Liu et al., 2012). Concentrations of Cd in homogenous material (polymer matrix) as reported by the producer range from 300 to 5000 mg/kg. A part of the waste or sorted waste particles could be drifted to incineration.

4.2.2 Waste management without component recovery

WEEE handled as mixed waste may be crushed and placed in landfills or possibly incinerated, resulting in slow leaching of cadmium from the polymer matrix after the glass shell has broken or atmospheric emissions.

4.2.3 Illegal waste management

Unaccounted-for WEEE may end up dumped in the environment or illegally exported outside the EU. As illegal export of WEEE is largely driven by the value of materials the waste contains, it will probably be sorted and in part recycled or reused, but the handling of the waste and the deposition of unwanted fractions is unlikely to appropriately consider human health and environmental considerations, particularly in developing countries.

4.2.4 Exposure assessment

Human exposure scenarios

Consumer exposure

Quantum dot products are not likely to be handled or mechanically treated or otherwise modified by a consumer in such a way that cadmium could be released. Therefore, consumer exposure to cadmium during the use of these products is not likely. Similarly, exposure of consumers to cadmium released to the environment from these products as a consequence of end-of-life or recycling operations is very unlikely. Also, the total amounts of cadmium related to this type of use are relatively low, only 20 µg per unit in lighting bulbs and 1 mg in a large TV display.

Occupational exposure

Occupational exposure to cadmium from quantum dot products could potentially take place during end-of-life or recycling operations, but only under exceptional circumstances. Worst case scenarios could include release of cadmium as a consequence of fire or inhalation of dust formed from crushed material. As pointed out above, the total amount of cadmium in these products is rather low, 20 µg in a lighting bulb or 1 mg in a large TV display. The occupational exposure limit of cadmium is 0.02 mg/m³, which is equivalent with the amount of cadmium in a lighting bulb per cubic meter (20 µg/m³). It is unlikely that such a high dust concentration could be formed in a realistic occupational exposure scenario, and according to unpublished test data available to the applicant, the production of inhalable dust in abrasive treatment of the material is negligible because of particle size distribution. For comparison, nickel–cadmium batteries, the major source of cadmium directed to landfills or recycling, contain up to 18% of cadmium. In quantum dot lighting devices and displays, cadmium concentrations are maximally 5000 ppm or 0.5%. Therefore the theoretical risk for occupational cadmium exposure due to quantum dot products is insignificant as compared with operations with nickel-cadmium batteries.

Environmental exposure

Assuming that broken components (as components on their own or e.g. crushed WEEE) are placed in a landfill or illegally in the environment, leaching of Cd is eventually likely to occur from the exposed polymer. Exposed to environmental conditions for an extended time, the polymer matrix appears to slowly release Cd in soluble (and therefore bioavailable) form as a degradation product of the nanoparticle material within (Liu et al., 2012). Unpublished leaching test data for the lighting and display products, available to the applicant, indicate that cadmium was not detected in the leachate (TCLP, EPA Method 1311). Another route of environmental exposure are atmospheric emissions from the incineration of waste containing the component (or, to a minor extent, accidental

fires). However, flue gases from incineration are washed in order to remove particulate pollutants. For EU limit values regarding cadmium emissions from waste incineration plants and leaching from landfill waste, see Table 1.

Table 1. The current EU limit values for cadmium in emissions from waste incineration plants and leaching from landfill waste.

Parameter	Limit value for Cd
Average air emission limit value for waste incineration plants over a sampling period of 30 min – 8 h ¹	0.05 mg Cd and Tl/Nm ³
Emission limit value for discharges of waste water from the cleaning of waste gases (Cd and Cd compounds) ¹	0.05 mg Cd/l
Leaching limit values for waste acceptable at landfills for inert waste ²	0.03 mg/kg dry substance (liquid-to-solid ratio 2 l/kg) 0.04 mg/kg dry substance (L/S = 10 l/kg) 0.02 mg/l (first eluate of percolation test at L/S = 0,1 l/kg)
Leaching limit values for granular waste acceptable at landfills for non-hazardous waste ²	0.6 mg/kg dry substance (liquid-to-solid ratio 2 l/kg) 1 mg/kg dry substance (L/S = 10 l/kg) 0.3 mg/l (first eluate of percolation test at L/S = 0,1 l/kg)
Leaching limit values for granular waste acceptable at landfills for hazardous waste ²	3 mg/kg dry substance (liquid-to-solid ratio 2 l/kg) 5 mg/kg dry substance (L/S = 10 l/kg) 1.7 mg/l (first eluate of percolation test at L/S = 0,1 l/kg)

¹ Directive 2010/75/EU of the European Parliament and of the Council on industrial emissions (integrated pollution prevention and control)

² Council Decision of 19 December 2002 establishing criteria and procedures for the acceptance of waste at landfills pursuant to Article 16 of and Annex II to Directive 1999/31/EC

5 COMPARISON OF DISPLAY OPTIONS

Potential toxic emissions during use and waste management and energy consumption during use, comparing the proposed and prevalent technologies of color conversion in displays backlit by LEDs, are summarized in Table 2.

Table 2. Comparison on Cd-containing and current technology in LED backlighting.

Parameter	LED backlighting with Cd-containing QD	LED backlighting with REM downconversion	Comments
Toxic emissions /exposures during use	Only accidental, fires	Only accidental	REMs are at solid state, chemically relatively stable oxides; relatively nontoxic (see 2.2).
Toxic emissions /exposures during waste management	If Cd not appropriately recovered: incineration (Cd predominantly remains in ash and ends up in landfill) or deposit in landfill, eventual leaching probable	If REMs not appropriately recovered: potential of REM emissions to the environment, probable destination landfill	
Energy consumption in use	More energy-efficient than conventional LEDs with REM downconversion		Reduction of energy consumption for identical brightness up to 20 % (estimated by applicant)

6 COMPARISON OF LIGHTING OPTIONS

Potential toxic emissions during use and waste management and energy consumption during use, comparing the proposed LED lights with Cd-based color conversion and fluorescent lighting, are summarized in Table 3.

Table 3. Comparison on Cd-containing LEDs with fluorescent lamps.

Parameter	LED with Cd-containing QD	Fluorescent lighting	Comments
Toxic emissions /exposures during use	Only accidental, fires: Cd	Only accidental: Hg	Mercury (Hg) is will vaporize from a broken lamp, highly toxic; Cd
Toxic emissions /exposures during waste management	If Cd not appropriately recovered: incineration (Cd predominantly remains in ash and ends up in landfill) or deposit in landfill, eventual leaching probable	If Hg not appropriately recovered: Hg emissions into the environment	tightly bound in a solid matrix as a solid compound
Energy consumption in use	More energy-efficient than conventional LEDs	Less energy-efficient than conventional LEDs	Significant reduction in energy consumption

7 SUMMARY AND CONCLUSIONS

By improving the efficiency of LED lights so that less energy is needed to produce identical brightness, quantum dot downconversion materials containing cadmium reduce the energy consumption of LCD displays (televisions, computer monitors, tablets, mobile phones), compared to backlighting of these consumer electronics by LED lights using rare-earth metals as downconversion material (the prevalent new technology). Reduction of energy consumption is greater if fluorescent lamps, which are less efficient than conventional LED lights (though currently in more extensive use in the EU as compared to LEDs due to other product characteristics), are replaced by LED lighting using the Cd-containing component. Fluorescent lamps also contain toxic mercury, which unlike the solid and tightly bound cadmium in the quantum dot nanocomposites is gaseous and easily released into the environment if the lamp breaks in use or is inappropriately handled during waste management.

Contribution of the planned use of cadmium containing quantum dot downconversion materials in lighting and displays to the total cadmium emissions and human exposure in Europe can be assessed by comparing the estimated amounts of cadmium in the products with the current emissions. The best estimate by QD Vision for the total amount of cadmium entering the EU in their products is less than 50 kg, which is less than 10 kg per year. Assuming the cadmium emission of 100 tonnes per year in the EU (see above), the imported cadmium, if emitted into the environment, is less than 0.01% of this amount. In the quantum dot downconversion materials in lighting and displays cadmium will be inside a solid material and therefore not easily released to the environment even if not recycled according to the current standards and regulations, differing from vaporization and release of mercury from fluorescent lamps. The assumed life cycle of displays and lighting is likely to be fairly long, and these products are efficiently recycled in the EU as indicated by the continuously decreasing emission and atmospheric deposition trends. Therefore, the estimated contribution of cadmium imported to the EU will be negligible. Furthermore, it is highly unlikely that cadmium in these products would end up in human food. Overall, cadmium emissions and human exposure show currently a clear decreasing trend.

Assuming generation of 26 % of electricity by coal power and 20 % reduction of energy consumption due to the use of LEDs provided with the Cd-containing quantum dot downconversion component, it can also be argued that since coal power also produces Cd emissions (coal assumed to contain 1-2 ppm Cd), the use of the component leads to a net reduction of Cd emissions. It should be noted that since average values for the EU are used regarding the proportion of coal power, the balances calculated are valid on the EU level, not regionally or locally.

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