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# Supplemental Statement on Life Cycle Analysis and Comparison of Cadmium (CASRN 7440-43-9, EC 231-152-8), Cadmium Selenide (CASRN 1306-24-7, EC 215-148-3) vs. Indium Phosphide (CASRN 22398-80-7, EC 244-959-5) for Color Conversion in Displays

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QD Vision, Inc.

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# Contents

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# 1 Goal Definition

This is an expert statement intended to update and supplement the previously submitted *Expert statement on LCA of Cd vs. non-Cd options for colour conversion in displays and lighting systems* by Linnunmaa, dated December 20, 2012 (Linnunmaa report). This document will supplement that prior Life Cycle Assessment (LCA) by providing additional information on cadmium selenide (CdSe) (Chemical Abstracts Service Registry Number (CASRN) 1306-24-7, EC 215-148-3), the substance that forms the basis of quantum dots (QD) produced by QD Vision, Inc. (QDV), and comparing these data with cadmium (Cd) (CASRN 7440-43-9, EC 231-152-8) and indium phosphide (InP) (CASRN 22398-80-7, EC 244-959-5) in display units. InP is included in this document because it is the only QD alternative to CdSe known to be currently on the market in displays or TVs. The assessment is based on available information in the public literature and information gathered by QDV and/or its consultants to include: a compare and contrast of the toxicology, potential exposure, QD product description, use, end of life (waste management), color performance differences, and cost implications including energy consumption advantages. Wherever possible, this document attempts to align with the principles of the "ILCD Handbook. Recommendations for Life Cycle Impact Assessment in the European Context" published by the Joint Research Centre.[1]

This statement is provided in support of an application by QDV for renewal of Exemption 39 under Directive 2011/65/EU (RoHS II – Restriction of Hazardous Substances), restricting the use of certain hazardous substances, including Cd, in electric and electronic equipment.

# 2 Background

QDV manufactures CdSe QDs. These are incorporated into optic devices. Manufacture of the QDs and optic devices takes place outside of the European Union (EU) and is not expected to relocate to the EU. Once the optic devices are manufactured, there is no potential for exposure to CdSe QDs under normal use, so even if displays were assembled in the EU, there would not be exposure or concomitant risk to workers, consumers, or the environment. The vast majority

[1] European Commission-Joint Research Centre (2011): Institute for Environment and Sustainability: International Reference Life Cycle Data System (ILCD) Handbook - Recommendations for Life Cycle Impact Assessment in the European context. First edition, November 2011. EUR 24571 EN. http://eplca.jrc.ec.europa.eu/uploads/ILCD-Recommendation-of-methods-for-LCIA-def.pdf.

of displays and TVs are assembled outside of the EU. Displays, including computer monitors and TVs using QDV's CdSe QDs are currently on the market in the EU. As such, the assessment of the impacts of CdSe QDs in the EU is limited to the use and disposal of displays and TVs under normal use.

## 2.1 The Product

QDV produces an optical component of a light-emitting diode (LED) lighting system used in liquid crystal displays (LCD) and TVs. In general, LCDs use a light source of one color in concert with other material to "down-convert" that source color into the broad spectrum necessary for accurate and appealing color performance in displays. Prior to the advent of LED/LCD technologies, LCD devices were lit by mercury-containing compact fluorescent (CFL) bulbs and used inorganic phosphors to down-convert the fluorescent light into the broader spectrum of colors for display. LEDs are solid state and more durable than mercury-containing CFL-type bulbs that routinely break from shock to the display or during disassembly. Use of LEDs enables a more efficient light source while eliminating the potential for the bulb to break and release mercury.

LEDs also provide an opportunity for better color-converting materials. In particular, the light from blue LEDs can be down-converted into the other necessary colors; the challenge is to convert the source light with high efficiency and excellent control of the color.

QDs have proven to be very effective down-converting materials. QDs are extremely small spheres of an inorganic material, often contained within a shell of another inorganic material, with an additional surface coating, or ligand.

The core and shell provide the critical down-conversion properties both in terms of energy efficiency and color. The ligand allows the core/shell structure to be dispersed in another medium. By adjusting the ligand, QDs can be made more or less biocompatible, *e.g.*, in medical applications, surface coatings are used to make QDs more biocompatible.

In QDV's optic component, the core/shell QD structure is coated with a ligand that allows the inorganic QDs to be dispersed in organic, high molecular-weight polymers. Once dispersed, the QDs cannot be mechanically isolated from the polymer -- separation requires chemical destruction of the polymer -- therefore the QD-polymer matrix meets the definition of a "homogenous material" according to the Restriction of Hazardous Substances (RoHS). The homogeneous material is then hermetically sealed in glass to form an optic device. The optic device is incorporated into the display unit along with the LED light source and other

components. The QD-polymer matrix and glass encapsulation ensures even distribution of the QDs in the optic, protects the QD from environmental degradation from oxygen, heat, or humidity, and prevents releases of, or exposures to, the QD material.

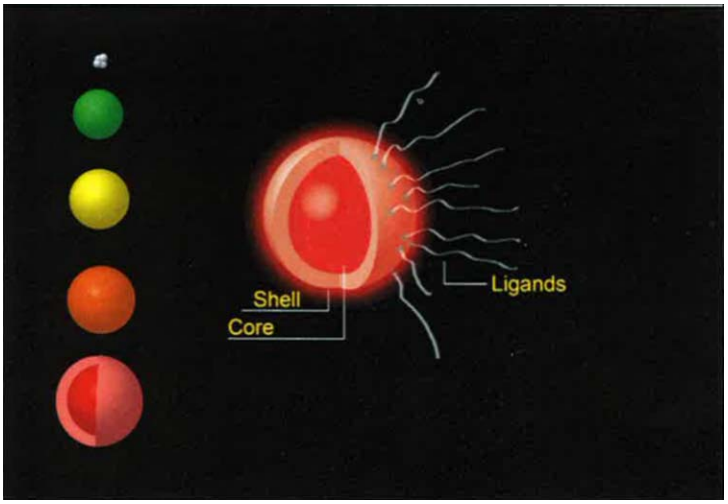


Figure 1: Schematic representation of core-shell-ligand quantum dot.

QDV produces QDs that are the most efficient down-converting materials available on the market in terms of energy efficiency, stability, and broad-spectrum color performance. After extensive research and testing, including work with alternative semiconductor materials such as indium, QDV concluded that the maximum benefit, both in terms of energy efficiency and broad-spectrum color performance, can only be achieved using a CdSe core with a cadmium zinc sulfide shell and a lipophilic surface modifier (ligand); together, these form a CdSe QD. The color performance is controlled by varying the size of the CdSe QD by taking advantage of the quantum effects that are present in materials with a very small size.

It is critical to note that the core/shell/ligand CdSe QDs have properties that are distinct from CdSe as well as Cd or other Cd-containing compounds. Furthermore, the CdSe QDs are not released from the optic except at end-of-life during recycling or recovery, or during improper disposal, such as incineration.

## 2.2 Toxicology

### 2.2.1 Cadmium

Information on Cd was provided in the prior LCA document.[2] Data on Cd in this section are presented to facilitate comparison with CdSe and InP.

#### 2.2.1.1 Physicochemical Properties

Elemental Cd (CASRN 7440-43-9, EC 231-152-8) is a transition metal with atomic number 48 and occurs in the 0 and +2 oxidation states. It is soluble in acid but insoluble in water. Because it readily reacts with other elements, Cd is rarely found in its elemental form but rather coupled with other elements in compounds such as cadmium oxide (CdO), cadmium chloride ($CdCl_2$) and cadmium sulfate ($CdSO_4$).[3] Table 1 summarizes differences in solubility between Cd and several Cd compounds.

**Table 1: Cd and Certain Cd Compounds**

| Ranking of Water Solubility | Name | CASRN | Formula | Soluble | Insoluble |
|---|---|---|---|---|---|
| Very soluble | Cd sulfate | 10124-36-4 | $CdSO_4$ | Water (540 g/L) | Alcohol, acetate, $NH_3$ |
| | Cd chloride | 10108-64-2 | $CdCl_2$ | Water (470 g/L) , acetone | Ethanol |
| Slightly soluble | Cd carbonate | 515-78-0 | $CdCO_3$ | Acids, $NH_4$ salts, KOCN | Water (3.2 mg/L), $NH_3$ |
| | Cd | 7440-43-9 | Cd | Acids, $(NH_4)(NO_3)$ | Water (2.3 mg/L) |
| | Cd oxide | 1306-19-0 | CdO | Acids, $NH_4$ salts, alkalies | Water (2.1 mg/L) |
| Insoluble | Cd sulfide | 1306-23-6 | CdS | Acids, $NH_3$ | Water (0.61 ng/L) |

[2] QD Vision, Inc./Linnunmaa (2012): Expert statement on LCA of Cd vs. non-Cd options for colour conversion in displays and lighting systems. December 20, 2012. http://rohs.exemptions.oeko.info/fileadmin/user_upload/RoHS_IX/Request_2013-2/A11_Linnunmaa_Expert_Statement_on_LCA.pdf.

[3] U.S. Environmental Protection Agency (2012): Cadmium Fact Sheet (CAS No. 7440-43-9). http://www.epa.gov/osw/hazard/wastemin/minimize/factshts/cadmium.pdf. Accessed 10/26/2015.

| Ranking of Water Solubility | Name | CASRN | Formula | Soluble | Insoluble |
|---|---|---|---|---|---|
| | Cd telluride | 1306-25-8 | CdTe | insoluble | Water (19 µg/L), |
| | Cd selenide | 1306-24-7 | CdSe | insoluble | Water |

### 2.2.1.2 Toxicokinetics

Should exposure to Cd occur, ingestion and inhalation would be the primary routes of potential human absorption of Cd. Absorption of Cd via the dermal route is negligible. Differences in absorption and distribution lead to different effect levels. For inhalation exposure, particle size and solubility in biological fluids are the more important determinants of the toxicokinetics. For oral exposure, most experimental studies have used soluble Cd compounds, which exist as the Cd(II) ion regardless of the initial salt.

Cd compounds have varied absorption rates that relate to the availability of Cd(II) ions and route of exposure. Toxicity of Cd compounds is primarily related to availability and absorption of Cd(II) ions. Cd compounds, similar to other metals as supported in *US Environmental Protection Agency's Framework for the Risk Assessment of Metals and Metal Compounds,* vary in toxicity with the principle of the higher the water solubility, the higher the toxicity. CdO and $CdCO_3$ are slightly water soluble but soluble in acids and therefore, are expected to release significant amount of Cd(II) ions at gastric pHs, while CdSe and CdTe are practically insoluble, with water solubility in the low ppb (part per billion) range. Although the dissolution of insoluble Cd particles is enhanced both at acidic pH and under aerobic conditions due to their thermodynamic properties, the absorption of insoluble Cd compounds through lungs and gastrointestinal tract is very limited.

The absorption of insoluble Cd particles from the lungs is more effective than that from the gastrointestinal tract due to the aerobic condition and acidic condition of the alveolar microphage lysosome in the lung. The deposition of inhaled Cd particles in different regions of the respiratory tract depends on particle size. The retention kinetics of inhaled Cd particles depends on the deposition in the respiratory tract and *in vivo* (lung) solubility.[4] CdSe particles are

[4] Oberdörster, G. (1992): Pulmonary deposition, clearance and effects of inhaled soluble and insoluble cadmium compounds. *IARC Sci Publ*, 118, 189-204.

insoluble in the lung and those deposited in the pulmonary region are cleared mainly via phagocytic uptake by alveolar macrophages.

Once absorbed Cd(II) ions are widely distributed in the body and are accumulative. Cd has a half-life of 20-30 years in humans due to its low rate of excretion with only 0.005-0.02% excreted in urine and feces each day.[5] Cd accumulates primarily in liver and kidneys with accumulation also in muscle and bone.

### 2.2.1.3 Toxicity

Most available experimental animal studies are based on the well-characterized Cd compounds such as CdO, CdS, $CdCO_3$, $CdCl_2$, and $CdSO_4$, where the toxicity is driven by the Cd(II) ions. In addition, there is a significant amount of data in the literature on observations of Cd exposure in humans.

Varied health effects are noted due to exposure to Cd(II) ions. Cd damages the lungs when inhaled. Acute high-dose or chronic exposures to Cd are associated with renal toxicity in humans once a critical body burden is reached. Cd(II) ions are genotoxic and carcinogenic,[6,7] An increased lung tumor rate was observed after inhalation exposure to $CdCl_2$ CdO, $CdSO_4$, or CdS aerosols in rats. Occupational cohort studies suggest that chronic exposure to Cd (primarily CdO) is strongly correlated with increased cancer incidence in the lung, prostate, and genitourinary system.[8,9,10] Epidemiological studies suggest that intake of Cd in the form of Cd(II) ions through diet is associated with a higher risk of endometrial, breast, and prostate

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5 Agency for Toxic Substances and Disease Registry (ATSDR) (2012). Toxicological Profile for Cadmium. http://www.atsdr.cdc.gov/toxprofiles/tp5.pdf. Accessed October 26, 2015.

6 Huff J., Lunn L.M., Waalkes M.P., Tomatis L., Infante P.F. (2007): Cadmium-induced Cancers in Animals and in Humans. *Int J Occup Environ Health*, 13(2),202–212.

7 Luevano J., Damodaran C. (2014): A Review of Molecular Events of Cadmium-Induced Carcinogenesis. *J Environ Pathol Toxicol Oncol,* 33, 3, 183–194.

8 Oberdörster, G. (1992): Pulmonary deposition, clearance and effects of inhaled soluble and insoluble cadmium compounds. *IARC Sci Publ*, 118, 189-204.

9 International Agency for Research on Cancer (IARC) (1993): Cadmium and cadmium compounds. *IARC Monogr Eval Carcinog Risks Hum*, 58, 119–237.

10 International Agency for Research on Cancer (IARC) (2012): *IARC Monogr Eval Carcinog Risks Hum,* 100C, 121–145.

cancer as well as to osteoporosis in humans. Many agencies, including the International Agency for Research on Cancer (IARC), National Institute of Occupational Safety and Health (NIOSH), U.S. Environmental Protection Agency (EPA), American Conference of Governmental Industrial Hygienists (ACGIH), and National Toxicology Program (NTP) have classified Cd as either a human carcinogen or probable human carcinogen.

Cd(II) ions may be a reproductive toxin. Some studies have found that animals exposed to high levels of Cd had a higher incidence of premature birth, low birth weight, stillbirth and spontaneous abortion. Animal studies also suggest that Cd exposure is linked to behavioral problems and learning disabilities.[11]

Cd is also an environmental hazard and can bioaccumulate in the ecosystem. Crops treated with Cd-containing fertilizer or commercial sludge can accumulate above-normal Cd concentrations and pass them on through the food web to higher organisms such as livestock and humans[12] The Joint Food and Agriculture Organization (FAO)/World Health Organization (WHO) Expert Committee on Food Additives (JECFA) has established 25 μg/kg body weight (bw)/month as tolerable Cd intake and 7 μg/kg bw of Cd as a provisional tolerable weekly intake (PTWI) level. The European Food Safety Authority (EFSA) has set 2.5 μg/kg body weight of Cd as a tolerable weekly intake for humans. Under EPA regulations, Cd in public drinking water supplies cannot exceed 5 ppb. The U.S. Food and Drug Administration (FDA) limits the amount of Cd in food colors to 15 parts per million (ppm). The Occupational Safety and Health Administration (OSHA) has set the permissible exposure limit (PEL) for Cd at a time-weighted average (TWA) of 0.005 ppm and limit for the amount of Cd in workplace air at 5 $\mu g/m^3$. The immediately dangerous to life and health (IDLH) level for Cd is 9 $mg/m^3$ according to NIOSH.

#### 2.2.1.4 Classification

Under Regulation (EC) No 1272/2008 (CLP) and associated ECHA guidelines, Cadmium (CASRN 7440-43-9) is classified as a member of generic substances of Cd metal in accordance with Annex VI as a Carcinogen Category 1B, Mutagen Category 2, Reproductive toxicity Category 2, Inhalation toxicity Category 2, Specific Target Organ Toxicity (STOT), Repeated

[11] U.S. Environmental Protection Agency (2012): Cadmium Fact Sheet (CAS No. 7440-43-9). http://www.epa.gov/osw/hazard/wastemin/minimize/factshts/cadmium.pdf. Accessed 10/26/2015.

[12] European Food Safety Authority (EFSA) (2012): Cadmium dietary exposure in the European population. *EFSA Journal,* 10, 1, 2551.

exposure Category 1, Acute aquatic toxicity Category 1 and Chronic aquatic toxicity Category 1.[13]

### 2.2.2 Cadmium Selenide

#### 2.2.2.1 Physico-Chemical Properties

CdSe (CASRN 1306-24-7; EC number 215-148-3) is a black to red-black, translucent, adamantine crystals used in the manufacture of II-IV semiconductor material. The general properties of CdSe are expected to be similar to CdTe because of the similar properties of tellurium and selenium, both of which are members of the chalcogen family.

#### 2.2.2.2 Toxicokinetics

CdSe is stable and the release of Cd(II) ions is very small in the absence of electron acceptors under reducing conditions. CdSe is subject to photo- and air-oxidation, generating free radicals[14,15,16,17]: therefore, gradual dissolution of CdSe can occur in the presence of electron acceptors such as oxygen gas. Dissolution of CdSe is pH-dependent, but the dissolution rate of CdSe is very low even under the most favorable acidic pH and/or aerobic conditions.[18,19]

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[13] European Chemicals Agency (ECHA): Classification, Labeling, and Packaging (CLP) Harmonized Classification for Cadmium (non-pyrophoric); EC Number 231-152-8. http://echa.europa.eu/information-on-chemicals/cl-inventory-database/-/cl-inventory/view-notification-summary/51061. Accessed 10/19/2015.

[14] Zeng C., Ramos-Ruiz A., Field J.A., Sierra-Alvarez R. (2015): Cadmium telluride (CdTe) and cadmium selenide (CdSe) leaching behavior and surface chemistry in response to pH and O2. *J Environ Manage*, 154, 78-85.

[15] Ipe B.I., Lehnig M., Niemeyer C.M. (2005): On the generation of free radical species from quantum dots. *Small*, 1, 706–709.

[16] Green M., Howman E. (2005): Semiconductor quantum dots and free radical induced DNA nicking. *Chem Commun*, 7, 121–123.

[17] Anas A., Akita H., Harashima H., Itoh T., Ishikawa M., Biju V. (2008): Photosensitized breakage and damage of DNA by CdSe/ZnS quantum dots. *J Phys Chem B*, 112, 10005–10011.

[18] Xi L., Lek J.Y., Liang Y.N., Boothroyd C., Zhou W., Yan Q., Hu X., Chiang F.B.Y., Lam Y.M. (2011): Stability studies of CdSe nanocrystals in an aqueous environment. *Nanotechnology,* 22, 1-5.

CdSe, however, has even lower dissolution rate than CdTe and therefore will be less bioavailable resulting in lower toxicity. Using supporting data from CdTe to assist in assessing CdSe toxicity therefore will result in a conservative estimate and classification for CdSe.[20]

### 2.2.2.3 Toxicity

There is not a significant amount of information on the toxicity and health effects of exposure to CdSe in the public literature. It is generally assumed that systemic toxicity of Cd compounds is attributed to the Cd(II) ion. A few existing studies indicate that the oral bioavailability of CdSe is very low and its adverse health effects depend primarily on Cd(II) ions released from CdSe and free radicals generated from photo- and air oxidation of CdSe. A 28-day oral (sub-chronic) study in rats showed that CdSe did not cause any toxic effect at doses of 30, 300 and 1,000 mg/kg/day[21]. No chronic studies are available on CdSe. The absorption of inhaled CdSe particles is expected to be very low due to its very stable nature with a very low dissolution rate even under the most favorable acidic and/or aerobic conditions.

Medical research is on-going regarding QDs that contain CdSe as part of an uncoated QD core. These QDs are being chemically modified for medical purposes by increasing their solubility and the biocompatibility. In a study with rat hepatocytes the intracellular release of Cd(II) ions via surface oxidation of the uncoated core CdSe-QDs was observed along with cytotoxicity, which is consistent with toxicity of other substances that release Cd(II) ions.[22]

CdSe is not yet registered under the European Union's Registration, Evaluation, Authorization and Restriction of Chemicals (REACH) regulation due to its low production and import volume and that its hazard profile does not dictate an earlier registration[23]. To date, it is unclear if CdSe

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19 Zeng C., Ramos-Ruiz A., Field J.A., Sierra-Alvarez R. (2015): Cadmium telluride (CdTe) and cadmium selenide (CdSe) leaching behavior and surface chemistry in response to pH and O2. *J Environ Manage*, 154, 78-85.

20 Ibid.

21 Kim Y.S., Song M.Y., Kim J.S., Rha D.S., Jeon Y.J., Kim J.E., Ryu H.Y., Yu I.J., Song K.S. (2009): 28-Day Oral Toxicity of Cadmium Selenide in Sprague-Dawley Rats. *Toxicol Res,* 25(3), 140-146.

22 Derfus A.M., Chan W.C.W., Bhatia SN. (2004): Probing the Cytotoxicity of Semiconductor Quantum Dots. *Nano Letters*, 4(1), 11–18.

23 Substances classified as CMR1/2 or R50/53(100t/y+)need to be registered before 30 November 2010, in accordance with REACH and REACH Guidance on Registration, Section 2.3. http://echa.europa.eu/documents/10162/13632/registration_en.pdf

will be registered under REACH. A comprehensive hazard and risk assessment of CdSe is not available under the EU regulatory framework. On the other hand, CdTe has been registered under REACH and a brief summary of the properties, toxicity and classification is presented in Annex 1 to supplement the toxicity data available on CdSe.

### 2.2.2.4 Classification

CdSe is not specifically identified in Annex VI, Table 3.2 of the Classification, Labeling and Packaging (CLP) regulation, rather its classification is based on the categories of "cadmium compounds" and "selenium compounds."

Based on the CLP classification principles and considering the 28-day rat oral study, CdSe could be classified as Acute inhalation and dermal toxicity Category 4, Acute aquatic Category 1 and Chronic aquatic Category 1. CdSe is classified as much less hazardous as the classification for Cd itself as noted in Sections 2.2.1.4 and 2.2.5.

More importantly, the homogenous material is the appropriate level for classification. The homogenous material in QDV's optic tube placed in display units has been determined by multiple RoHS testing laboratories to be the polymer matrix with <0.2% w/w Cd in CdSe QDs, with no detectible residual free Cd. At this level, none of the thresholds for the various toxicity endpoints are triggered,. Considering the hazard classes and assuming that the polymer itself is not classified, the overall classification for the homogenous material is **not classified**.

## 2.2.3 Indium Phosphide

### 2.2.3.1 Physicochemical properties

Indium (In; CASRN 7440-74-6, EC 231-180-0) is a soft silver-white post-transition metal with atomic number 49 and occurs in the 0 as well as +1, +2 and +3 oxidation states. In(I) and In(II) compounds tend to disproportionate into the In(III) compounds and In metal. Only In(III) compounds are stable in aqueous systems.[24]

InP (CASRN 22398-80-7, EC 244-959-5) forms black cubic crystals, insoluble in water and slightly soluble in mineral acids. It can react with moisture or acids producing hydrogen,

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[24] Slattery J.A. (1995): *Kirk-Othmer Encycl Chem Tech*, 14, 158-159.

phosphorus and phosphine ($PH_3$); when heated to decomposition, it may emit toxic fumes of POx[25]. InP is used in the manufacture of III-V semiconductor materials.

### 2.2.3.2 Toxicokinetics

The absorption and distribution of In is highly dependent on its chemical form. InP is soluble in simulated gastric fluid and hardly soluble in simulated lung fluids[26].

InP is poorly absorbed when ingested with most being excreted in the feces. In oral toxicity experiments in mice and rats, less than 0.67 percent of the dose was retained in tissues or urine following 24 hours and there was no clear relationship between the dose and biological effects. The orally absorbed In was evenly distributed among the major organs and was not accumulating in the bodies of rats following multiple dosing. The urinary elimination half time was determined to be about 321 hours in rats.[27]

When inhaled, InP particles, following phagocytic uptake by alveolar macrophages, could be solubilized within the cell through the phagolysosomal acidification pathway resulting in cell death and the subsequent release of In(III) ions extracellularly by the dying cells.[28] Following intratracheal administration of InP particles to mice and rats, systemic absorption of In was detected in serum, liver, spleen and testes, but the toxicity was much lower than that of more soluble compounds, such as $InCl_3$ and $In(NO_3)_3$ except for toxic effects in the lungs. As

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25 International Agency for Research on Cancer (IARC) (2006): *Monographs on the Evaluation of the Carcinogenic Risk of Chemicals to Humans,* 86, 197-224. http://monographs.iarc.fr/ENG/Monographs/vol86/mono86-9.pdf. Accessed October 26, 2015.

26 Kabe I., Omae K., Nakashima H., Nomiyama T., Uemura T., Hosoda K., Ishizuka C., Yamazaki K., Sakurai H. (1996): In vitro solubility and in vivo toxicity of indium phosphide. *J. Occup. Health*, 38, 6-12.

27 National Toxicology Program (2001): NTP Technical Report on the Toxicology & Carcinogenesis Studies of Indium phosphide (CAS No. 22398-80-7) in F344/N Rats and B6C3F1 Mice (Inhalation studies). NTP TR 499, NIH Publication No. 01-4433. https://ntp.niehs.nih.gov/ntp/htdocs/lt_rpts/tr499.pdf. Accessed October 26, 2015.

28 Gwinn W.M., Qu W., Bousquet R.W., Price H., Shines C.J., Taylor G.J., Waalkes M.P., Morgan D.L. (2015): Macrophage solubilization and cytotoxicity of indium-containing particles as in vitro correlates to pulmonary toxicity in vivo. *Toxicol Sci*, 144, 1, 17-26.

expected, the majority of the tissue In was in the lungs with lung clearance half-life of 0.4 – 6.6 years and less than 0.36 percent of the dose being evenly distributed to the other major organs.[29]

The excretion routes of In vary depending on the form. Ionic In is transported in the blood bound to plasma proteins such as transferrin and albumin, accumulated in lysozymes of the proximal tubules of the kidney as insoluble phosphate salts, and subsequently excreted via urine. Colloidal In is eliminated primarily in feces.[30]

### 2.2.3.3 Toxicity

InP was shown to cause pulmonary inflammation associated with oxidative stress, epithelial cell damage, and lung, adrenal and liver cancers when administrated via inhalation in experimental animals[31,32,33]. Mild eye irritation may result from exposure to its dust or vapor. In(III) ions can be toxic to liver and kidney when given by injection in animals, but oral In compounds do not have the chronic toxicity of salts of heavy metals, probably due to poor absorption in basic conditions. Ionic In is concentrated in the kidneys, producing renal failure; colloidal In is taken up by the reticuloendothelial system, causing damage to the liver and spleen. Ionic In has been shown to produce marked ultrastructural damage to the endoplasmic reticulum of both hepatocytes and renal proximal tubule cells, with associated disruption of heme metabolism and hemoprotein function.

In the NTP carcinogenicity study in mice and rats by inhalation exposure to InP, there was an increased incidence of alveolar/bronchiolar carcinomas in male mice and alveolar/bronchiolar adenomas and carcinomas in female mice and male and female rats. There was also a significant

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[29] International Agency for Research on Cancer (IARC) (2006): *Monographs on the Evaluation of the Carcinogenic Risk of Chemicals to Humans,* 86, 197-224. http://monographs.iarc.fr/ENG/Monographs/vol86/mono86-9.pdf. Accessed October 26, 2015.

[30] Fowler B.F., Maples-Reynolds N. (2015): Indium. In Nordberg G.F., Fowler B.F., Nordberg M. (eds.), *Handbook on the Toxicology of Metals* (4th edition), Academic Press, 845–853.

[31] Kabe I., Omae K., Nakashima H., Nomiyama T., Uemura T., Hosoda K., Ishizuka C., Yamazaki K., Sakurai H. (1996): In vitro solubility and in vivo toxicity of indium phosphide. *J Occup Health*, 38, 6-12.

[32] Gottschling B.C., Maronpot R.R., Hailey J.R., Peddada S., Moomaw C.R., Klaunig J.E., Nyska A. (2012): The role of oxidative stress in indium phosphide-induced lung carcinogenesis in rats. *Toxicol Sci*, 64, 1, 28-40.

[33] Oda K. (1997): Toxicity of a low level of indium phosphide (InP) in rats after intratracheal instillation. *Ind Health*, 35, 1, 61-68.

increase in the incidence of hepatocellular adenomas/carcinomas in exposed mice and an increased incidence of benign and malignant pheochromocytomas of the adrenal gland in rats. Other findings were marginal increases in the incidences of adenomas/carcinomas of the small intestine in male mice, mononuclear-cell leukaemia in rats, fibroma of the skin in male rats and carcinoma of the mammary gland in female rats.

InP was concluded as being a probable human carcinogen based on the well-conducted two-year inhalation bioassay studies in experimental animals by NTP.[34,35,36] Analysis of genetic alterations in InP-induced hepatocellular adenomas and carcinomas revealed increases of mutation frequency in β-catenin.[37] Several studies[38,39] suggested that InP-induced oxidative stress may play an important role in the pulmonary carcinogenesis of InP. There are two cohort studies reporting cancer incidence increased in workers of semiconductors industry, and InP is one of the possible carcinogens. One study showed increased incidences of skin and rectum

[34] International Agency for Research on Cancer (IARC) (2006): *Monographs on the Evaluation of the Carcinogenic Risk of Chemicals to Humans,* 86, 197-224. http://monographs.iarc.fr/ENG/Monographs/vol86/mono86-9.pdf. Accessed October 26, 2015.

[35] NTP Technical Report on the Toxicology & Carcinogenesis Studies of Indium phosphide (CAS No. 22398-80-7) in F344/N Rats and B6C3F1 Mice (Inhalation studies). NTP TR 499, NIH Publication No. 01-4433, 2001: https://ntp.niehs.nih.gov/ntp/htdocs/lt_rpts/tr499.pdf. Accessed October 26, 2015.

[36] Fowler B.F., Maples-Reynolds N. (2015): Indium. In Nordberg G.F., Fowler B.F., Nordberg M. (eds.), *Handbook on the Toxicology of Metals* (4th edition), Academic Press, 845–853.

[37] International Agency for Research on Cancer (IARC) (2006): *Monographs on the Evaluation of the Carcinogenic Risk of Chemicals to Humans,* 86, 197-224. http://monographs.iarc.fr/ENG/Monographs/vol86/mono86-9.pdf. Accessed October 26, 2015.

[38] Ibid.

[39] Gottschling BC, Maronpot RR, Hailey JR, Peddada S, Moomaw CR, Klaunig JE, Nyska A. (2001): The role of oxidative stress in indium phosphide-induced lung carcinogenesis in rats. *Toxicol Sci*, 64(1), 28-40.

cancers in workers at West Midlands, England.[40,41] The other showed increased incidences of lung and stomach cancers in female workers in Scotland.[42]

As to potential effects on fertility, there are no multi-generation reproductive toxicity studies available. However, repeated dose toxicity studies in hamsters via intra-tracheal instillation showed a decreased sperm count, decreased weights of testes and epididymes, and histopathological lesions in the testes. InP was also shown to accumulate in the rat testis following inhalation exposure. In addition, intravenous administration of ionic In to pregnant rats, mice and hamsters has been reported to produce teratogenic and/or embryolethal effects.[43]

As little is known about its ecological fate of In, bioaccumulation has not been ruled out. Occupational exposure limits for In set by ACGIH, NIOSH and agencies around the world is 0.1 $mg/m^3$ time-weighted average of threshold limit value (TLV) or recommended exposure limit (REL).[44]

InP is under consideration for inclusion as a restricted substance[45] on Annex II of RoHS.

#### 2.2.3.4 Classification

InP was subject to harmonized classification proposal sponsored by France and reviewed by the Risk Assessment Committee in 2009 in association with EU CLP regulation[46]. The harmonized

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40 Sorahan T, Pope DJ, McKierman MJ. Cancer incidence and cancer mortality in a cohort of semiconductor workers: an update. *British Journal of Industrial Medicine*. 49, 215-216.

41 Nichols L, Sorahan T. Cancer incidence and cancer mortality in a cohort of UK semiconductor workers, 1970-2002. (2005): *Occup Med* 55, 8, 625-630.

42 McElvenny DM, Darnton AJ, Hodgson JT, Clarke SD, Elliott RC, Osman J. (2003): Investigation of cancer incidence and mortality at a Scottish semiconductor manufacturing facility. *Occup Med,* 53, 419-430.

43 Fowler B.F., Maples-Reynolds N. (2015) Indium. In Nordberg G.F., Fowler B.F., Nordberg M. (eds.), *Handbook on the Toxicology of Metals* (4th edition), Academic Press, 845–853.

44 International Agency for Research on Cancer (IARC) (2006): *Monographs on the Evaluation of the Carcinogenic Risk of Chemicals to Humans,* 86, 197-224. http://monographs.iarc.fr/ENG/Monographs/vol86/mono86-9.pdf. Accessed October 26, 2015.

45 Öko-Institut e.V. & Eunomia (2014): Study for the Review of the List of Restricted Substances under RoHS 2 – Analysis of Impacts from a Possible Restriction of Several New substances under RoHS 2. Available at http://www.oeko.de/oekodoc/2046/2014-627-en.pdf

classification of InP is Carcinogen Category 1B, Reproductive toxicant Category 2, and Specific target organ toxicity (STOT) – repeat exposure (RE) Category 1.

### 2.2.4 Summary of Toxicology Comparison of Cadmium, Cadmium Selenide, and Indium Phosphide

In summary, key elements of the toxicity and respective classification of Cd, CdSe and InP are as follows:

- Cd(II) ions released from Cd compounds have chronic toxicity and carcinogenic effects, therefore, those Cd compounds that could release meaningful amount of Cd(II) ions are probable human carcinogens and have been classified under CLP accordingly.
- CdSe is insoluble with an extremely low dissolution rate. Although CdSe has not been tested for chronic effects, in a 28-day oral study it had a NOAEL of greater than 1,000 mg/kg/day. Data on a suitable read-across substance, CdTe (see Annex 1 for additional information) has a more robust data set than CdSe and supports the principle that the insoluble forms with extremely low dissolution rates of Cd do not have the same classification as Cd. CdSe is not classified for chronic health effects, including carcinogenicity, under CLP.
- InP has been tested in a 2-year bioassay (chronic study) and is a probable human carcinogen. It has been classified under CLP accordingly.

[46] European Chemicals Agency (ECHA) (2009): Proposal for Harmonised Classification and Labelling. Indium Phosphide. http://echa.europa.eu/documents/10162/7564f5ed-a09c-41a0-b8ee-7aebf4287c99. Accessed October 26, 2015.

## 2.2.5 Summary of Classification Comparison

| **Name** | **Formula** | Hazard Class – Harmonized Annex VI of CLP regulation | CLP Hazard Statement code(s) | Other Classification based on CLP principles |
|---|---|---|---|---|
| Cd* (7440-43-9) | Cd | Carc. 1B, Muta. 2, Repr. 2, Acute Tox (inhl). 2, STOT RE 1, Aquatic Acute 1, Aquatic Chronic 1 | H350, H341, H361fd, H330, H372, H400, H410 | |
| Cd and its compounds* | CdX | Acute (oral) Cat 4, Acute (dermal) Cat 4, Acute (inhalation) Cat 4, Acute aquatic Cat 1, Chronic aquatic Cat 1 | H332, H312, H302, H400, H410 | |
| Cd selenide (1306-24-7) | CdSe | | | Acute (inhalation) Cat 4, Acute (dermal) Cat 4, Aquatic Acute Cat 1, and Aquatic Chronic Cat 1 |
| CdSe QD in homogenous material | | Not classified | -- | Not classified |
| Cd telluride (1306-25-8) | CdTe | | | Acute (inhl) Cat 4, Aquatic Chronic Cat 2 |
| Indium phosphide | InP | Carc. Cat 1B Repro Cat 2 , STOT RE 1 | H350, H361f, and H372 | |

*Cd and its compounds is not fully defined and therefore, it is not clear which Cd substances are contained within this grouping. The Annex VI table indicates Cd compounds does not include Cadmium sulphoselenide, reaction mass of cadmium sulphide with zinc sulphide, reaction mass of cadmium sulphide and mercury sulphide as these are specified in the Annex.

H350:  May cause cancer.

H341:  May cause genetic defects.

H361f:  May damage fertility.

H361fd:  May damage fertility. May damage the unborn child.

H330:  Fatal if inhaled.

H332:  Harmful if inhaled

H302:  Harmful if swallowed

H312:  Harmful in contact with skin

H372:  Causes damage to organs through prolonged or repeated exposure.

H400:  Very toxic to aquatic life.

H410:  Very toxic to aquatic life with long lasting effects

H411:  Toxic to aquatic life with long lasting effects.

# 3 Life Cycle Assessment – Cadmium Selenide and Indium Phosphide

QDs are incorporated into displays and TVs through one of two methods: in a plastic film covering the full size of the display and placed behind the LCD screen, or an on-edge plastic/glass optical component placed above the LED light bar within the display backlight unit. The film requires significantly higher amounts of QDs than on-edge optics simply because of the much higher surface area of the film. As shown in Table 2, QD optic component loading is about 1.5 mg Cd per unit for a large display lit with an on-edge optical component, while an on-surface film for the same size display would require 162 mg Cd. Note that in either case, this is the total amount of Cd contained in the CdSe QD.

These loading levels of Cd overstate the exposure potential to a toxic form of Cd. Unlike CFL light sources, there is no mechanism for the release of the QD material from the display itself. The QD materials are non-volatile and are further incorporated into a polymer matrix as a homogenous material (and then either placed between low-permeability barrier films, or in the case of the on-edge optic manufactured by QD Vision, encapsulated in a hermetically-sealed glass tube).

An update of the estimate of the LCD TV market in the EU[47], calculates that if every one of the estimated 57.4 million LCD TVs expected to be sold in Europe in 2015 used on-edge CdSe QD optical components, 86 kg of additional Cd (as CdSe QDs) would enter the EU. A more realistic estimate of 35 percent market penetration would lead to about 30 kg of Cd (as CdSe QDs) entering the EU. To put this in perspective, in the Linnunmaa report, the authors calculated that there were 103 tonnes (103,000 kg) of Cd emissions reported in 2010, mostly from energy and metals (such as zinc) production. Even in a worst-case scenario of every TV using CdSe QDs and every TV being incinerated rather than being reused, recycled, or landfilled, the total Cd released in the EU would increase by less than 0.1 percent. Note that this calculation ignores the use-phase benefits of the highly efficient CdSe QD technology.

Currently, InP QDs used in displays are utilized in on-surface films, where approximately forty times as much QDs are required for effective performance then when compared to optic tubes. Table 3 compares quantities of Cd and InP entering into commerce in the EU based on 35% and 100% market penetration assumptions.

[47] Risk & Policy Analysts (2015): Cadmium Selenide Quantum Dots—RoHS Exemption Supporting Arguments. Final Report.

**Table 2: Comparative concentration and quantity of cadmium in various applications[48]**

| Product | Required Cd in the homogenous material | | Resulting Cd amount in product | | Comments |
|---|---|---|---|---|---|
| | On edge (QD Vision) | On surface (3M) | On edge (QD Vision) | On surface (3M) | |
| Large display | 1200 ppm | 90 – 45 ppm yellowish / low efficiency: 600 ppm (approximate film thickness: 400 µm) | 1.5 mg (1500 µg) | TVs: 8.5-40.4mg yellowish / low efficiency: 162 mg | TVs: Display sizes from 32" - 60"+ diagonal |
| Medium display | 2000 ppm | 150 – 250 ppm (approximate film thickness: 200 µm) | 0.2 mg (200 µg) | Monitors: 2.4-14.1mg Notebooks: 0.8-4.0mg Tablets: 0.07-1.4mg | Mid-size monitors, laptops, tablets Display size from 10-32" diagonal |
| Small display | 3000 ppm | 205 – 340 ppm (approximate film thickness 100 µm) | 10 µg | Mobile phones: 0.07-1.4mg | Smart phones Display size around 3" diagonal |

Source: Risk & Policy Analysts. (2015): Cadmium Selenide Quantum Dots—RoHS Exemption Supporting Arguments. Final Report.

**Table 3: Comparison of amounts of cadmium and indium phosphide required at various levels of market penetration.**

| Substance | Amount assuming 100% market adoption | Amount assuming 35% market adoption | |
|---|---|---|---|
| Cd (in CdSe QD on-edge components) | 86 kg | 30 kg | |
| InP (in In-based QD on-surface film) | 3,400 kg | 1,200 kg | Based on 40x loading[49] |

[48] Öko-Institut e.v, Fraunhofer IZM & Eunomia (2014): Assistance to the Commission on Technological Socio-Economic and Cost-Benefits Assessment Related to Exemptions from the Substance Restrictions in Electrical and Electronic Equipment (RoHS Directive) Final Report – Pack 4. Available at http://rohs.exemptions.oeko.info/fileadmin/user_upload/RoHS_IX/20140422_RoHS2_Evaluation_Ex_Requests_2013-1-5_final.pdf

[49] QD Vision (2015): Quantum Dot Displays – The Facts

## 3.1 Production

Detailed production methods on either CdSe or InP QDs are not available in the public domain, so comparison is not possible. Production of the QD optical components is expected to take place outside of the EU. Those components will be assembled into displays and TVs with most of the assembly occurring in Asia.

Although QD production methods cannot be compared, availability of metals can be. Cd has a mature recycling infrastructure, and 15% or more of Cd is recycled worldwide.[50] Cd is not considered a "critical raw material" and supply is expected to remain plentiful. In contrast, indium has been identified as a "critical raw material" by the EC[51] because of its growing use in electronics, photovoltaic and other applications. Unfortunately, there is little, if any indium recycling, with recycling limited to recovery of industrial production waste[52]. Increasing demand, coupled with heavy dependence on imports from China, which is the largest supplier of indium, can lead to a significant supply risk. An estimate of the indium demand from In-based QDs suggests an increase of "just 15%" compared to standard LCD displays.[53] Fifteen percent is not a negligible increase in demand and could easily lead to substantially more expensive QDs and other products relying on indium as supplies are stressed.

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[50] United Nations Environment Programme (2011): Recycling Rates of Metals, A Status Report (ISBN: 978-92-807-3161-3). http://www.unep.org/resourcepanel/Portals/24102/PDFs/Metals_Recycling_Rates_110412-1.pdf. Accessed October 26, 2015.

[51] European Commission (2014): Press Release – 20 critical raw materials – major challenge for EU industry. http://europa.eu/rapid/press-release_IP-14-599_en.htm. Accessed October 26, 2015.

[52] Gensch C.O., Baron Y., Blepp M., Bukne D., Moch K. (2014): Study for the Review of the List of Restricted Substances under RoHS 2 – Analysis of Impacts from a Possible Restriction of Several New Substances under RoHS 2, Öko-Institut e.v. http://www.oeko.de/oekodoc/2046/2014-627-en.pdf. Accessed October 26, 2015.

[53] Nanoco & Dow (2013): Response to RoHS Exemption Application N$^{o}$ 2013-2. Available at http://rohs.exemptions.oeko.info/fileadmin/user_upload/RoHS_IX/Request_2013-2/20131106_Nonoco_Dow_Contribution_Ex_2013-2_Response_to_RoHS_Questionnaire.pdf. Accessed October 26, 2015.

## 3.2 Use (Energy Efficiency)

Previous analysis concluded that the use phase is the single most important life-cycle phase in terms of environmental impact due to the electricity consumption.[54] Although stand-by mode does consume some energy, the vast majority of power consumption is the result of display use in the on-mode. Power consumption depends on a wide variety of components, including lighting, semiconductor components, network components, sound amplifier, and the power transformer. Down-converting material, such as QDs or phosphors, do not draw power directly, but do contribute to overall energy efficiency through the efficiency of converting the light source to the appropriate colors. Luminance and color gamut are the key performance properties and to the extent that down-conversion materials can achieve those properties with less light input from the light source, less energy is required overall. It is important to recognize that to properly analyze the relative energy efficiency of optical components, one must control for differences in the other components of a TV.

In its meta-analysis of the energy use reports, RPA found substantial energy savings from CdSe QD technologies over both compact fluorescent and other QD technologies.[55] A better, direct comparison between In-based and CdSe-based QD technologies is available in QD Visions benchmarking report[56]. They measured the energy use and display performance for two comparable 55" TVs: one (a Samsung model UN55JS9000F) that relies on InP QD film and one (a Hisense model LED55XT910X3DUC) that uses a CdSe QD film. As shown in Table 4, the two TVs, as manufactured, had similar luminance, with the Hisense unit having about 1 percent higher luminance, while consuming 10 percent less energy. Overall the as-manufactured Hisense (CdSe QD) TV had about 12 percent better luminance efficiency and covered a greater percentage of the color gamut (as a percentage of the NTSC Area). These two units are quite comparable, with a slight edge to the Hisense CdSe TV in terms of luminance, efficiency and color gamut. However, as noted above, to properly understand the role of the QD film, other components must be kept the same. In this case, QD Vision swapped the QD films from the two

[54] Fraunhofer IZM (2007): EuP Preparatory Studies "Televisions" (Lot 5) – Final Report on Task 1 "Definition". http://www.eup-network.de/fileadmin/user_upload/Produktgruppen/Lots/Final_Documents/Lot_5_Final_Report_1-8.pdf. Accessed October 26, 2015.

[55] Risk & Policy Analysts (2015). Cadmium Selenide Quantum Dots—RoHS Exemption Supporting Arguments. Final Report.

[56] QD Vision (2015): Benchmarking Report.

TVs and re-measured the luminance, power consumption, and color gamut. Not surprisingly, the power consumption by the two TVs is largely unchanged since all the components that draw energy remained the same in each TV; the QD film does not draw power itself, it only converts in incipient light energy to a different wavelength. Rather than showing up in the power consumption of the display, the efficiency of the QD film is reflected in the luminance and color gamut. In these two measures, it becomes clear how much of a difference a CdSe QDs make in the energy and color performance. The Hisense TV with an In-based QD film showed a nearly 23 percent drop in luminance and luminance efficiency along with a 9 percent drop in color gamut. The In-based QD film simply does not convert the incipient light to luminance and broad spectrum color as efficiently. Conversely, the Samsung TV with a CdSe QD film showed a 32 percent increase in luminance and luminance efficiency over the baseline In-based QD film while improving color gamut coverage by about 10 percent. This experiment makes it clear that there are substantial performance gains, in terms of luminance, color gamut, and energy efficiency when using CdSe QDs rather than In-based QDs. Manufacturers of TVs using In-based QDs may be able to come close to the performance of CdSe QD-based TVs, but their color gamut performance and energy efficiency could be substantially better if they used CdSe QDs.

**Table 4: Benchmarking comparison of Hisense TV with CdSe QD film and Samsung TV with In-based QD film.**[57]

| TV | QD film | Luminance (nits) | Power (W) | Luminance Efficiency (nits/W) | NTSC Area (1931) |
|---|---|---|---|---|---|
| Hisense (as manufactured) | CdSe-based | 520 | 189.9 | 2.74 | 97.1% |
| Samsung (as manufactured) | In-based | 515 | 210.0 | 2.45 | 91.7% |
| Hisense | In-based | 402 | 189.7 | 2.12 | 87.9% |
| Samsung | CdSe-based | 680 | 209.1 | 3.25 | 101.3% |

[57] QD Vision (2015): Benchmarking Report.

Depending on the baseline selected, CdSe QDs improve energy efficiency by approximately 20-30 percent when compared to In-based QD TVs. Using the mid-point 25 percent improvement and emission rates calculated in the RPA analysis allow a calculation of the benefits related to the energy savings, as shown in Table 5.

**Table 5: Lifetime emissions reductions for CdSe QD TVs compared to In QD TVs**

| Benefit | Lifetime reductions per TV (based on 2013 emission rates) | Total savings in EU (35% market penetration) |
|---|---|---|
| $CO_2$ emissions | 436 kg $CO_2$ eq. | 8.7 billion kg CO2 eq. |
| Cadmium emissions | 1.3 mg | 24 kg |
| Mercury emissions | 3.0 mg | 61 kg |
| Lead emissions | 17.8 mg | 356 kg |
| SOx emissions | 230 g | 4.6 million kg |
| NOx emissions | 210 g | 4.2 million kg |
| $PM_{10}$ emissions | 15 g | 300,000 kg |

Assumptions: 25% improvement in energy efficiency (CdSe QD TV vs In QD TV), 30,000 hour (20.5 yr) lifetime for each TV, and 35% market penetration (20 million TVs in EU). Emission rates from RPA document.[58]

The calculations shown in Table 5 demonstrate the significant benefits that may be achieved by employing CdSe QDs in TVs when considered relative to In-based CFQDs. Note that the amount of Cd that is avoided over the life of a TV (1.3 mg) is about the same amount of Cd used in a TV (1.5 mg). The Cd emissions from electrical generation is a dispersive release of a bioavailable form (as Cd(II) ions), whereas the CdSe QDs have very low solubility and, because they are entrained in the optical component, are non-dispersive.

[58] Risk & Policy Analysts (2015). Cadmium Selenide Quantum Dots—RoHS Exemption Supporting Arguments. Final Report.

## 3.3 End of Life

According to an analysis by RPA[59] [58]collection rates for information technology (IT) and telecommunication equipment and consumer equipment is, on average, over 80 percent being collected for recycle or reuse in 2013. The remaining WEEE is either: 1) collected by unregistered enterprises and properly treated; 2) collected by unregistered enterprises and improperly treated or even illegally exported abroad; or 3) disposed of as part of residual waste (e.g. to landfills or incinerators).

The RPA analysis concludes that "occupational exposure to CdSe and InP is likely to be negligible during normal WEEE processing conditions."[60]

### 3.3.1 Take Back and Recovery of Isolated Components

The information above suggests that display devices in the EU are likely to be recycled or reused. There is currently no established system in Europe for the recycling of indium from WEEE, with total end-of-life recycling rates at less than 1%.[61]

In comparison, Cd recycling is mature with 15% or more of Cd used in the world recycled.

### 3.3.2 Waste Management Without Component Recovery

If displays are not reused or disassembled for recycling, the most likely disposal pathway is landfill, but some may be incinerated. If landfilled, the QDs are unlikely to leach out from the device because the ligands on the surface of the QDs are designed to maximize compatibility between the QD and the solid polymer matrix in which they are dispersed. Toxicity Characteristic Leaching Protocol (TCLP) simulates leaching of toxic chemicals through a landfill and, in the case of televisions that may be improperly disposed, did not detect any trace of Cd during the testing of the QD optics[62]. TCLP data for indium-based QDs are not available.

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59 Risk & Policy Analysts. (2015): Cadmium Selenide Quantum Dots—RoHS Exemption Supporting Arguments. Final Report.

60 Ibid.

61 Buchert M., Manhart A., Bleher D., Pingel D. (2012): Recycling critical raw materials from waste electronic equipment, Öko-Institut e.v. Available at: http://www.oeko.de/oekodoc/1375/2012-010-en.pdf.

62 Per third-party testing. A complete report of the TCLP results is available from QD Vision upon request.

Incineration is more problematic. Incineration of a QD optic is expected to destroy the polymer and convert the core CdSe material to a CdO compound that will become part of the incinerator ash. Generally waste incinerators have excellent ash controls and release little solid material in the flue gas. Assuming ninety percent removal of ash from flue gas, only 0.15 mg of Cd would be released by the incineration of a CdSe QD unit from a TV. As open, uncontrolled incineration is illegal in the EU and therefore extremely rare, this exposure pathway is not addressed.

## 3.4 Summary/Comparison of Display Options

Overall, while InP QDs provide some of the performance of CdSe QDs, there remains a significant, measurable advantage in the color performance and energy efficiency in using CdSe QDs in TVs and displays. Over the life of the TV, enough energy is saved, and associated emissions of heavy metals, NOx, SOx, and particulate matter avoided, to more than offset the amount of Cd contained in a TV. In addition, the form of Cd in the CdSe QDs is much less toxic than Cd or its soluble compounds. The trade-off is introducing a non-dispersive use of low-toxicity CdSe QDs to reduce dispersive emissions of Cd released during energy production. The reduction in releases of Cd, lead, mercury, arsenic, NOx, SOx, and $CO_2$ demonstrate the environmental and human health advantages of CdSe QDs over CFQDs. Alternative QDs use InP, which has been identified by the EHCA as a human carcinogen. Because InP QDs can only be used in on-surface films due to limits of their operating lifetime under heat and flux and, because of the much higher surface area, are used in much higher quantities than CdSe QDs in optics, and even then do not achieve the level of color gamut performance, luminance, and energy efficiency.

Furthermore, long-range supply of Cd is not threatened, while indium demand is growing significantly and is expected to come under increased pressure as other semiconductor uses grow. Such demand pressure will drive up the cost of In-based QDs, increasing further the cost/performance benefit of CdSe QDs.

# 4 Summary/Conclusion

Hazard data on CdSe is limited: CdSe has not been tested for chronic effects; however, in a 28-day oral study it had a NOAEL of greater than 1,000 mg/kg/day. CdSe is not classified for chronic health effects, including carcinogenicity, under CLP. By contrast, InP has been tested for chronic effects in a 2-year bioassay and is a probable human carcinogen; it has been classified under CLP accordingly.

Because of the difference in energy efficiencies between CdSe QDs and InP QDs, and their use in on-edge optics vs. film technologies in display applications, approximately 40-fold more InP would be expected to enter commerce.[63] At 35 percent market penetration, that amounts to 1,200 kg of InP as opposed to 30 kg of CdSe.

The energy efficiency differences between CdSe QDs and InP QDs would also result in significant decreases in environmental emissions of greenhouse gases and heavy metals when CdSe QDs are used as opposed to InP QDs. At 35% market penetration of displays and TVs:

- CdSe QDs are expected to save 24 kg of Cd(II) emissions annually. Assuming a worst case scenario where 100% of the CdSe in products was released into the environment as Cd(II) ions, a total of only 6 kg of Cd(II) ions would be released into the environment over the lifetime of all CdSe QD displays and TVs entering the market;
- CdSe QDs are expected to save 8.7 billion kg $CO_2$ eq. emissions;
- CdSe QDs are expected to save 61 kg mercury (Hg) emissions;
- CdSe QDs are expected to save 356 kg of lead (Pb) emissions; and
- CdSe QDs are expected to save 4.6 million, 4.2 million and 300,000 kg SOx, NOx and $PM_{10}$ emissions respectively.

Finally, Cd recycling and recovery systems are mature, with 15% or more of all Cd recycled. In, however, has little or no recycling; approximately 100% of all InP may be expected to eventually enter the environment and, as a critical material, supplies may be expected to diminish over time, with concomitant cost increases.

[63] This ratio would be expected to change to the extent CdSe QDs were introduced onto the market in films. Currently the QD Vision product is used in on-edge optics.

## Annex 1 – Supplemental Data on CdTe

Cadmium telluride (CdTe, CAS number 1306-25-8; EC number 215-149-9) is a Cd compound that is very similar, in terms of structure and properties, to CdSe. Most notably, both CdSe and CdTe are insoluble in water[64].

CdTe is registered under REACH and its data are available for review via the REACH dissemination site. Data available on the REACH dissemination site are not necessarily considered as publicly available data; however, the data are available to the European Commission, ECHA, and Member State Competent Authorities that may have similar responsibilities under RoHS. As such, we wish to direct reviewers to the assessment.

In addition, data are publicly available on CdTe via the Cd REACH Consortium website, http://www.reach-cadmium.eu/pg.php?id_menu=4

Recent toxicological research by Zayed and Philippe[65] and Kaczmar[66] differentiates CdTe from other Cd compounds. According to Held et al. (2012)[6768], the European Chemicals Agency (ECHA) no longer classifies CdTe as harmful if ingested nor harmful in contact with skin. CdTe

[64] Clever, H.L., M. Elizabeth Derrick, M. E., and Johnson, S.A. (1992): The Solubility of Some Sparingly Soluble Salts of Zinc and Cadmium in Water and in Aqueous Electrolyte Solutions., *J Phys Chem Ref Data*, 21, 5, 1992. http://www.nist.gov/srd/upload/jpcrd444.pdf. Accessed October 16, 2015.

[65] Zayed, J., and Philippe, S. (2009): Acute oral and inhalation toxicities in rats with cadmium telluride. *Intl J of Toxicology*, 28, 259-265.

[66] Kaczmar, S., (2011): Evaluating the read-across approach on CdTe toxicity for CdTe photovoltaics, SETAC North America 32nd Annual Meeting, Boston, November 2011.

[67] Chuangchote, S., Rachakornkij, M., Punmatharith, T., Pharino, C., Changul, C., Pongkiatkul, P. (2012): Review of Environmental, Health and Safety of CdTe Photovoltaic Installations throughout Their Life-Cycle. http://www.pv-thin.org/wp-content/uploads/2013/09/CdTe-peer-review_-Thailand.pdf. Accessed October 26, 2015.

[68] Held, M., Hagendorf, C., Bagdahn, J., and Wehrspohn, R. (2012): Scientific Comment of Fraunhofer to Life Cycle Assessement of CdTe Photovoltaics. http://www.csp.fraunhofer.de/presse-und-veranstaltungen/details/id/852/. Accessed October 26, 2015.

exhibits aqueous solubility and bioavailability properties that are approximately two orders of magnitude lower than $CdCl_2$, which means that CdTe does not readily release the $Cd^{2+}$ ions upon contact with water or biological fluids. Based on these results, the toxicity and environmental mobility of CdTe would be expected to be much lower than other forms of Cd[69]. Previously, Zayed and Philippe evaluated acute inhalation and oral toxicities of CdTe in rats and found the median lethal concentration and dose to be orders of magnitude higher than that of Cd.[70] Moreover, prior testing by Harris et al. (1994) showed no detectable effects of CdTe on male or female rat reproduction.[71]

The dissolution of Cd compounds is enhanced both at acidic pH and under aerobic conditions due to their thermodynamic properties. Based on the REACH registered substances information, the Cd released of total Cd content from CdTe is approximately 35, 0.1, 1, and 80% in gastric fluid, interstitial fluid, perspiration fluid and lysosomal fluid, respectively.

Once properly and securely captured and encapsulated, CdTe used in manufacturing processes may be rendered harmless. CdTe is less toxic than elemental Cd, at least in terms of acute exposure toxicity testing.[72]

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69 Ibid.

70 Zayed, J., and Philippe, S. (2009): Acute oral and inhalation toxicities in rats with cadmium telluride. *Intl J of Toxicology*, 28, 259-265.

71 Harris, et al., (1994): The general and reproductive toxicity of the photovoltaic material cadmium telluride(CdTe), *Toxicologist*, 14, 267, (abstract).

72 Zayed, J., and Philippe, S. (2009): Acute oral and inhalation toxicities in rats with cadmium telluride. *Intl J of Toxicology*, 28, 259-265.