Cadmium Telluride Panel Integrity and Safety
Executive Summary

- It is important to distinguish that Cadmium Telluride (CdTe) is not the same as free Cadmium.
- CdTe is a very stable compound that is non-volatile and non-soluble in water. The vapor pressure of CdTe at ambient conditions is zero. Therefore, it is impossible for any vapors or dust to be generated when using PV modules. CdTe has a melting point of 1041°C (1905 °F) and boiling point 1050^{o}C (1922°F).
- The panel's thin layer of CdTe is encapsulated between two sheets of glass and sealed with an industrial laminate, which further limits the potential for release into the environment in the event of breakage.
- Panel breakage is rare and occurs only in approximately 1% of modules over 25 years, or 0.04% per year. More than one-third of breakages occur during shipping and installation; therefore, the broken modules are removed prior to plant operation (First Solar).
- Panels are subject to a battery of reliability tests simulated for violent weather (heavy wind, rain, hail) to ensure integrity without damage in the field (https://www.youtube.com/watch?v=rtxgeCH31EI)
- Using the Toxicity Characteristic Leaching Procedure (TCLP), worst-case scenario modeling of total release (which is, again, very implausible) of CdTe (which is, again, very stable) from broken panels, estimated Cd concentrations in soil, groundwater, and air to be below health screening levels, background levels, and common levels in agricultural fertilizers. (Sinha et al. 2012)
- It's worth noting that the TCLP used in these analyses is very conservative, as it assumes the panels break into pieces and fall directly to the ground, which is not the case: field breakages mainly consist of various types of stress and impact fractures in which panels remain largely intact with a number of glass fractures or cracks, rather than break into pieces. (Sinha and Wade 2015)
- Multiple sources report that CdTe PV end-of-life or broken panels pass Federal (TCLP-RCRA) leaching criteria for non-hazardous waste. Therefore, panels could be disposed of in landfills (NC State 2017).
- Even in the case of a fire, research shows that less than 0.1% of the cadmium is released when a CdTe panel is exposed to fire. The fire melts the glass and encapsulates over 99.9% of the cadmium in the molten glass. (Fthenakis et al. 2005)

Regarding the bigger picture:

- CdTe panels do not result in more Cadmium in the environment.
- Substantial quantities of Cadmium are generated as a by-product of zinc production for steel products, regardless of how much Cadmium is used in PV. Encapsulating and stabilizing cadmium as CdTe in PV panels presents a safer option than its current uses, and is much more preferred to disposing it. (Fthenakis and Zweibel 2003)

- Phosphate fertilizers represent the major source of cadmium in agricultural soils and the combustion of fossil fuels represents the primary source of Cd emissions to air. (Six and Smolders 2014)
- Whenever CdTe PV replaces coal in power generation it lowers the associated Cd emissions to air by 100–360 times. (Raugei and Fthenakis 2010)

<u>Citations:</u>

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North Carolina State University Clean Energy Technology Center, "Health and Safety Impacts of Solar Photovoltaics". 2017

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<u>First Solar Panel Quality Assurance Video</u>

YouTube: "First Solar Module Reliability"
https://www.youtube.com/watch?v=rtxgeCH31EI

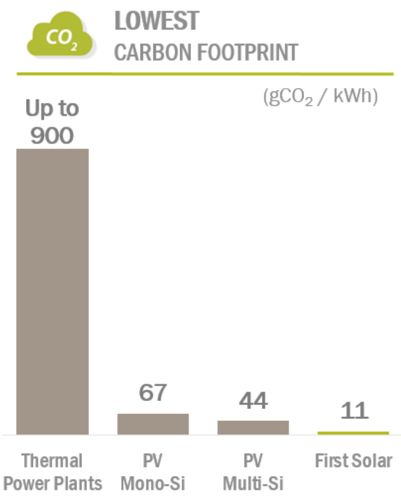
Appendix

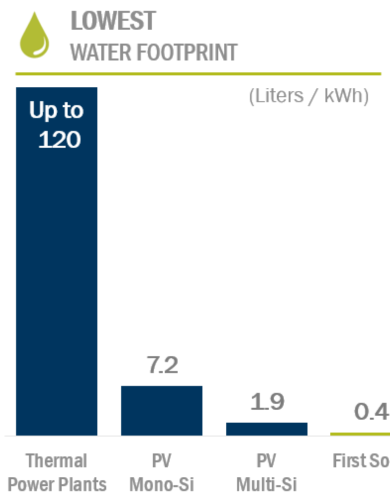
Cited Materials

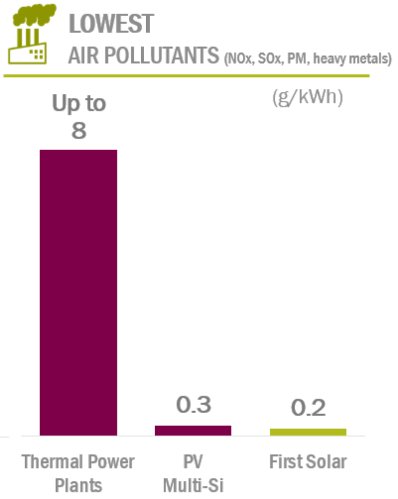
CdTe PV FAQ

What are the environmental benefits of First Solar's thin film PV technology?

First Solar's advanced thin film PV solutions are the industry's leading eco-efficient technology due to their superior energy yield, competitive cost and smallest life cycle environmental impacts. [1] By using less grid electricity during manufacturing, First Solar thin film modules have the smallest carbon footprint and lowest life cycle water use and air pollutants of any PV technology on the market. [2] [3] [4] [5] [6] According to a study by UNEP, CdTe PV has the lowest life cycle human health and ecological impacts of all PV technologies per kWh of electricity produced. [7]

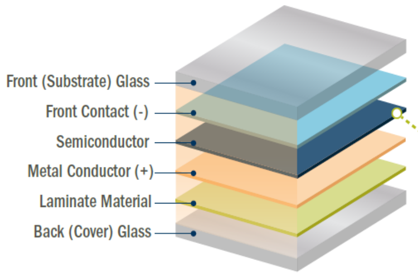


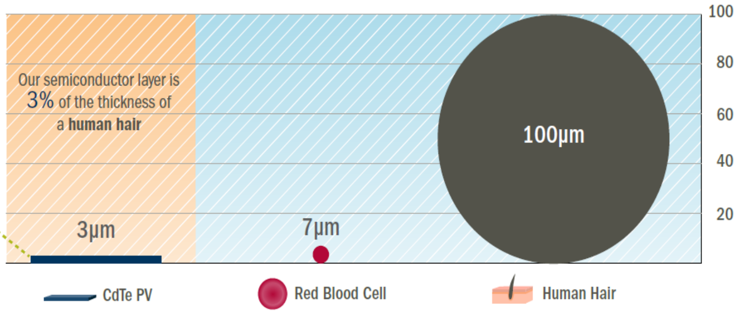




What is cadmium telluride (CdTe)?

CdTe is a semiconductor material used in First Solar PV modules that is ideal for absorbing and converting sunlight into electricity. Because CdTe is almost perfectly matched to the solar spectrum, First Solar modules require 98-99% less semiconductor material than conventional crystalline silicon modules. The semiconductor layer in First Solar modules is a few microns thick, equivalent to 3% the thickness of a human hair or less than half the thickness of a red blood cell.





Is CdTe the same as cadmium?

No, third-party research studies have shown that CdTe differs from cadmium (Cd) due to its extremely high chemical and thermal stability. [8] CdTe is a stable compound that is insoluble in water, has a melting point (1041°C) and boiling point (1050^{0}C), and a low evaporation rate. In addition, First Solar's thin film semiconductor is encapsulated between two sheets of glass and sealed with an industrial laminate, which further limits the potential for release into the environment in the event of fire or breakage.

SOLID AND STABLE COMPOUND

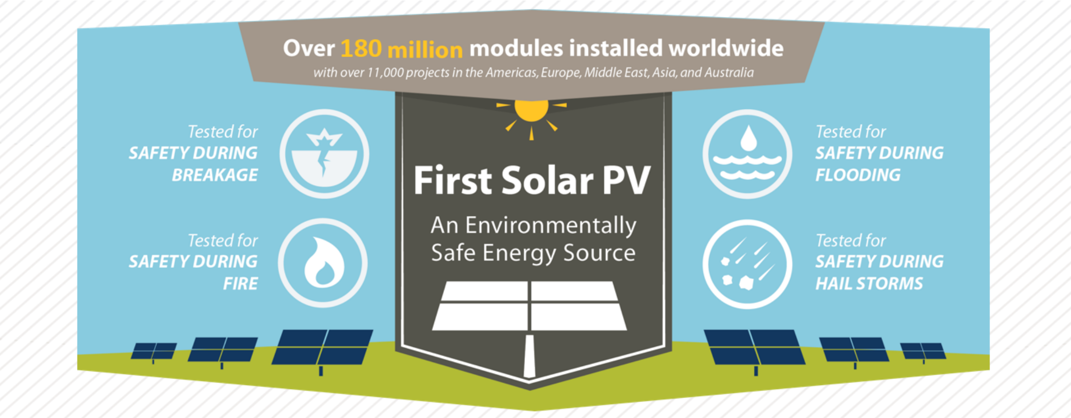
INSOLUBLE IN WATER

HIGH MELTING/ BOILING POINT

LOW VAPOR PRESSURE

Does CdTe PV technology pose a risk to human health or the environment?

No. More than 40 researchers from leading international institutions have confirmed the environmental benefits and safety of First Solar's thin film PV technology over its entire life cycle; during normal operation, exceptional accidents such as fire or module breakage, and through end-of-life recycling and disposal: http://www.firstsolar.com/Resources/Sustainability-Documents?ty=Peer+Reviews&re=&ln=%20. First Solar thin film modules have been tested for safety during breakage, fire, flooding and hail storms and meet rigorous performance testing standards, demonstrating their durability and reliability in real-world environments. With over 17,000 MW deployed worldwide, First Solar thin film modules have a proven record of safe and reliable performance.



"CdTe modules do not represent any risk for human health nor for the environment, during normal operating conditions and in the exceptional case of fire or breakage." [9]

- National Renewable Energy Centre (CENER)

"Research demonstrates that [CdTe PV modules] pose negligible toxicity risk to public health and safety while significantly reducing the public's exposure to cadmium by reducing coal emissions." [10]

–North Carolina State University

"…replacing coal generation with [CdTe] PV will prevent Cd emissions in addition to preventing large quantities of CO2, SO2, NOx, and particulate emissions." [11]

- National Renewable Energy Laboratory and Brookhaven National Laboratory

Are First Solar modules certified to EHS, quality and durability standards?

All First Solar manufacturing plants are certified to ISO 14001 for Environmental Management, ISO 9001 for Quality, and OHSAS 18001 for Occupational Health and Safety. First Solar modules are certified to regional standards including UL for North America, CEC for Australia, Golden Sun for China, MCS for the U.K. and JET for Japan. First Solar PV modules also meet rigorous performance testing standards, demonstrating their durability and reliability in real-world environments.

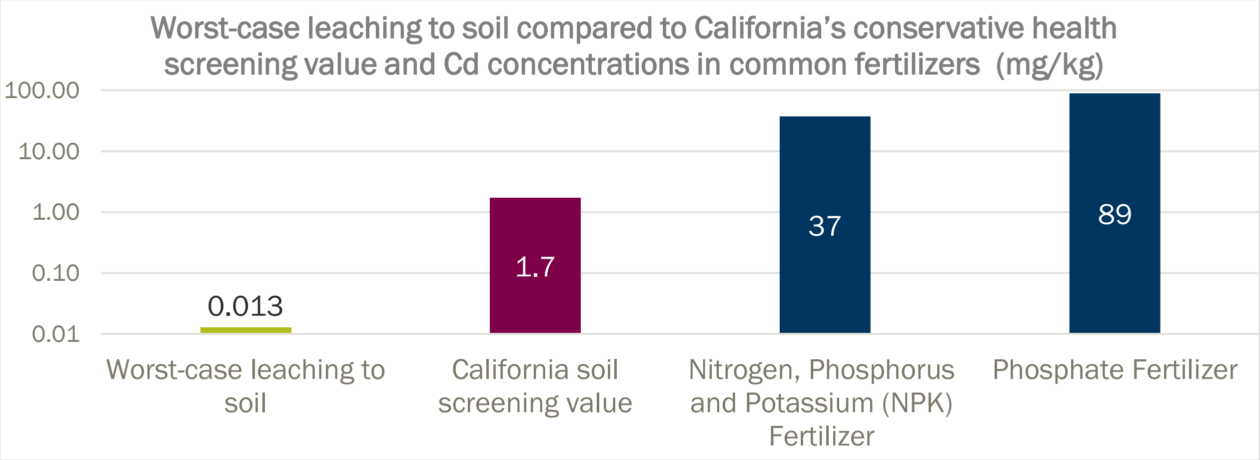
Test	Description	Results
IEC 61646/ IEC 61730 Certification	Basic industry market entry certifications	PASS *1500V certification level*
UL 1703	PV module electrical safety	PASS
Fire rating	Flammability testing	Class A Spread of Flame Class B Burning Brand
Thresher Test	Multiplies basic IEC 61730/61646 test cycles and durations 2X to 4X	PASS *<5% Power Output drop*
Long-Term Sequential Test	6-month accelerated protocol to evaluate long-term harsh climate durability	PASS *1st thin film module, and one of only 5 modules in the*
Atlas 25+ Certification	12-month weathering-intensive certification through projected 25+ year harsh climate field lifetimes	PASS *One of only 4 modules in the world to pass.*
IEC 62804 PID-Resistant Certification	Demonstrates high resistance to potential induced degradation at extreme ± 1500V voltages at most extreme 192hr 85C/85% RH test levels, enabling confident floating and grounded applications	PASS *1500V*
IEC 60068 Certification Desert Sand Resistance	Demonstrates minimal power loss and package integrity resistant to wind-blown particulates	PASS
Fraunhofer PV Durability Initiative	Durability benchmarking program rates modules according to their likelihood of performing reliably over their expected service life based on accelerated stress testing and long-term outdoor exposure	PASS *Best-in-class long term durability*
VDE Quality Tested	Quality certification for entire PV power plant enhances performance, ensures electrical and mechanical safety of the system and provides independent verification to investors, lenders and insurance companies.	PASS 1st PV company to achieve certification

What could happen if modules break?

Module breakage is rare and occurs only in approximately 1% of modules over 25 years or 0.04% per year. More than one-third of breakages occur during shipping and installation, therefore the broken modules are removed prior to plant operation. During operation, most breakages consist of impact fractures in which the module is still bound together by the industrial laminate.

Even in a worst-case leaching scenario, which assumes all the CdTe from broken modules were to leach as cadmium into the rainfall, Cd concentrations in soil, air, and groundwater are still below conservative human health screening levels in California. [12]

Modelled results for worst-case leaching to soil are up to 7,000 times lower than cadmium concentrations in common fertilizers.



What could happen in the event of a fire?

Independent analysis indicates potential Cd emissions from CdTe PV modules involved in a fire would be negligible as the majority of CdTe would remain encapsulated in glass. Heating experiments simulating residential fires showed that 99.96% of the Cd content of CdTe PV modules would be encapsulated in molten glass under the high temperatures of a building fire (800 to 1100˚C). [13] For ground-mount systems, the short-lived maximum fire temperatures (1000°C) are below the melting point of CdTe (1041°C), limiting release. [14] Even in a worst-case scenario that assumes a maximum Cd content (66.4 g/m^2) more than four times the amount of CdTe contained in First Solar modules, a large fire area, and the shortest distance from the emission site, the calculated Cd emission concentration is still below conservative air pollution exposure limits for the public and emergency responders. [15]

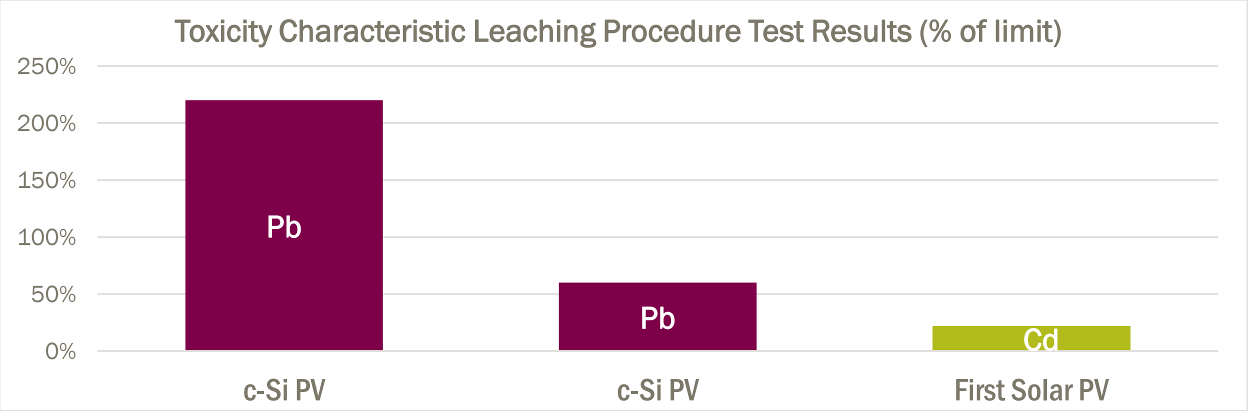
For perspective, potential accidental emissions occurring during fires are up to three orders of magnitude lower than routine emissions from coal and oil power plants. [16]

Does CdTe PV lead to an increase of cadmium in the environment?

No. Cadmium is generated as an unavoidable by-product of zinc production for steel products, regardless of its use in PV. Increased steel demand for building, construction and automobiles is expected to lead to a potential oversupply of cadmium. [17] When combined with tellurium, cadmium is converted into a stable compound, which is used to generate clean electricity for 25+ years. Cadmium exposure to the general population primarily occurs via smoking, followed by ingestion of Cd-containing food. Phosphate fertilizers represent the major source of cadmium in agricultural soils and the combustion of fossil fuels represents the primary source of Cd emissions to air. [18] [19] Whenever CdTe PV replaces coal in power generation it lowers the associated Cd emissions to air by 100–360 times. [20]

Does CdTe PV technology have unique end-of-life management requirements?

No. Responsible end-of-life management is important to the whole PV sector in order to maximize resource recovery and manage environmentally sensitive materials which are common in the industry. Both CdTe and crystalline silicon PV modules contain comparable quantities of heavy metals. Leaching tests results found that crystalline silicon PV modules released a range of 3-11mg/L of lead (Pb), which corresponds to 60%-220% of the federal U.S. waste characterization test (TCLP) limit. [21] Potential environmental impacts from end-of-life disposal of crystalline silicon PV modules are therefore comparable to or greater than that of CdTe PV.



Can First Solar modules and PV power plants be recycled at end-of-life?

Yes. Over 90% of a First Solar PV power plant is recyclable. First Solar has a long-standing leadership position in PV recycling and provides global PV module recycling services that enable PV power plant owners to meet their decommissioning and end-of-life (EOL) requirements simply, cost effectively and responsibly. First Solar's high-value recycling process recovers approximately 90% of the glass for reuse in new glass products and over 90% of the semiconductor material for reuse in new modules. The remainder of the recycled module scrap (approximately 5 to 10%) which cannot be used in secondary raw materials is handled using other responsible waste treatment and disposal techniques. Due to the shredding, crushing and heating typically involved in recycling processes, material losses are inevitable and the recovery ratio is always less than 100%. [22]

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NC CLEAN ENERGY TECHNOLOGY CENTER

NC STATE UNIVERSITY

Health and Safety Impacts of Solar Photovoltaics

The increasing presence of utility-scale solar photovoltaic (PV) systems (sometimes referred to as solar farms) is a rather new development in North Carolina's landscape. Due to the new and unknown nature of this technology, it is natural for communities near such developments to be concerned about health and safety impacts. Unfortunately, the quick emergence of utility-scale solar has cultivated fertile grounds for myths and half-truths about the health impacts of this technology, which can lead to unnecessary fear and conflict.

Photovoltaic (PV) technologies and solar inverters are not known to pose any significant health dangers to their neighbors. The most important dangers posed are increased highway traffic during the relative short construction period and dangers posed to trespassers of contact with high voltage equipment. This latter risk is mitigated by signage and the security measures that industry uses to deter trespassing. As will be discussed in more detail below, risks of site contamination are much less than for most other industrial uses because PV technologies employ few toxic chemicals and those used are used in very small quantities. Due to the reduction in the pollution from fossil-fuel-fired electric generators, the overall impact of solar development on human health is overwhelmingly positive. This pollution reduction results from a partial replacement of fossil-fuel fired generation by emission-free PV-generated electricity, which reduces harmful sulfur dioxide (SO_2), nitrogen oxides (NO_x), and fine particulate matter ($PM_{2.5}$). Analysis from the National Renewable Energy Laboratory and the Lawrence Berkeley National Laboratory, both affiliates of the U.S. Department of Energy, estimates the health-related air quality benefits to the southeast region from solar PV generators to be worth 8.0 ¢ per kilowatt-hour of solar generation.[1] This is in addition to the value of the electricity and suggests that the air quality benefits of solar are worth more than the electricity itself.

Even though we have only recently seen large-scale installation of PV technologies, the technology and its potential impacts have been studied since the 1950s. A combination of this solar-specific research and general scientific research has led to the scientific community having a good understanding of the science behind potential health and safety impacts of solar energy. This paper utilizes the latest scientific literature and knowledge of solar practices in N.C. to address the health and safety risks associated with solar PV technology. These risks are extremely small, far less than those associated with common activities such as driving a car, and vastly outweighed by health benefits of the generation of clean electricity.

This paper addresses the potential health and safety impacts of solar PV development in North Carolina, organized into the following four categories:

(1) Hazardous Materials
(2) Electromagnetic Fields (EMF)
(3) Electric Shock and Arc Flash
(4) Fire Safety

1. Hazardous Materials

One of the more common concerns towards solar is that the panels (referred to as “modules” in the solar industry) consist of toxic materials that endanger public health. However, as shown in this section, solar energy systems may contain small amounts of toxic materials, but these materials do not endanger public health. To understand potential toxic hazards coming from a solar project, one must understand system installation, materials used, the panel end-of-life protocols, and system operation. This section will examine these aspects of a solar farm and the potential for toxicity impacts in the following subsections:

(1.2) Project Installation/Construction
(1.2) System Components
    1.2.1 Solar Panels: Construction and Durability
    1.2.2 Photovoltaic technologies
        (a) Crystalline Silicon
        (b) Cadmium Telluride (CdTe)
        (c) CIS/CIGS
    1.2.3 Panel End of Life Management
    1.2.4 Non-panel System Components
(1.3) Operations and Maintenance

1.1 Project Installation/Construction

The system installation, or construction, process does not require toxic chemicals or processes. The site is mechanically cleared of large vegetation, fences are constructed, and the land is surveyed to layout exact installation locations. Trenches for underground wiring are dug and support posts are driven into the ground. The solar panels are bolted to steel and aluminum support structures and wired together. Inverter pads are installed, and an inverter and transformer are installed on each pad. Once everything is connected, the system is tested, and only then turned on.

Figure 1: Utility-scale solar facility (5 MW_{AC}) located in Catawba County. Source: Strata Solar

1.2 System Components

1.2.1 Solar Panels: Construction and Durability

Solar PV panels typically consist of glass, polymer, aluminum, copper, and semiconductor materials that can be recovered and recycled at the end of their useful life.[2] Today there are two PV technologies used in PV panels at utility-scale solar facilities, silicon, and thin film. As of 2016, all thin film used in North Carolina solar facilities are cadmium telluride (CdTe) panels from the US manufacturer First Solar, but there are other thin film PV panels available on the market, such as Solar Frontier's CIGS panels. Crystalline silicon technology consists of silicon wafers which are made into cells and assembled into panels, thin film technologies consist of thin layers of semiconductor material deposited onto glass, polymer or metal substrates. While there are differences in the components and manufacturing processes of these two types of solar technologies, many aspects of their PV panel construction are very similar. Specifics about each type of PV chemistry as it relates to toxicity are covered in subsections a, b, and c in section 1.2.2; on crystalline silicon, cadmium telluride, and CIS/CIGS respectively. The rest of this section applies equally to both silicon and thin film panels.

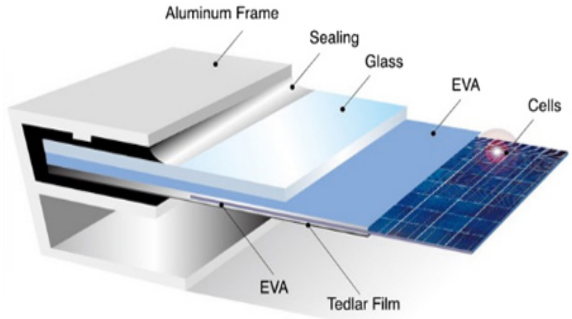

Figure 2: Components of crystalline silicon panels. The vast majority of silicon panels consist of a glass sheet on the topside with an aluminum frame providing structural support. Image Source: www.riteksolar.com.tw

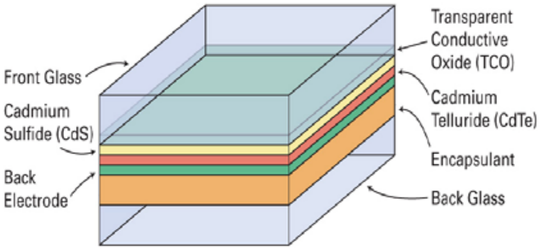

Figure 3: Layers of a common frameless thin-film panel (CdTe). Many thin film panels are frameless, including the most common thin-film panels, First Solar's CdTe. Frameless panels have protective glass on both the front and back of the panel. Layer thicknesses not to scale. Image Source: www.homepower.com

To provide decades of corrosion-free operation, PV cells in PV panels are encapsulated from air and moisture between two layers of plastic. The encapsulation layers are protected on the top with a layer of tempered glass and on the backside with a polymer sheet. Frameless modules include a protective layer of glass on the rear of the panel, which may also be tempered. The plastic ethylene-vinyl acetate (EVA) commonly provides the cell encapsulation. For decades, this same material has been used between layers of tempered glass to give car windshields and hurricane windows their great strength. In the same way that a car windshield cracks but stays intact, the EVA layers in PV panels keep broken panels intact (see Figure 4). Thus, a damaged module does not generally create small pieces of debris; instead, it largely remains together as one piece.

Figure 4: The mangled PV panels in this picture illustrate the nature of broken solar panels; the glass cracks but the panel is still in one piece. Image Source: http://img.alibaba.com/photo/115259576/broken_solar_panel.jpg

PV panels constructed with the same basic components as modern panels have been installed across the globe for well over thirty years.[3] The long-term durability and performance demonstrated over these decades, as well as the results of accelerated lifetime testing, helped lead to an industry-standard 25-year power production warranty for PV panels. These power warranties warrant a PV panel to produce at least 80% of their original nameplate production after 25 years of use. A recent SolarCity and DNV GL study reported that today's quality PV panels should be expected to reliably and efficiently produce power for thirty-five years.[4]

Local building codes require all structures, including ground mounted solar arrays, to be engineered to withstand anticipated wind speeds, as defined by the local wind speed requirements. Many racking products are available in versions engineered for wind speeds of up to 150 miles per hour, which is significantly higher than the wind speed requirement anywhere in North Carolina. The strength of PV mounting structures were demonstrated during Hurricane Sandy in 2012 and again during Hurricane Matthew in 2016. During Hurricane Sandy, the many large-scale solar facilities in New Jersey and New York at that time suffered only minor damage.[5] In the fall of 2016, the US and Caribbean experienced destructive winds and torrential rains from Hurricane Matthew, yet one leading solar tracker manufacturer reported that their numerous systems in the impacted area received zero damage from wind or flooding.[6]

In the event of a catastrophic event capable of damaging solar equipment, such as a tornado, the system will almost certainly have property insurance that will cover the cost to cleanup and repair the project. It is in the best interest of the system owner to protect their investment against such risks. It is also in their interest to get the project repaired and producing full power as soon as possible. Therefore, the investment in adequate insurance is a wise business practice for the system owner. For the same reasons, adequate insurance coverage is also generally a requirement of the bank or firm providing financing for the project.

1.2.2 Photovoltaic (PV) Technologies

a. Crystalline Silicon

This subsection explores the toxicity of silicon-based PV panels and concludes that they do not pose a material risk of toxicity to public health and safety. Modern crystalline silicon PV panels, which account for over 90% of solar PV panels installed today, are, more or less, a commodity product. The overwhelming majority of panels installed in North Carolina are crystalline silicon panels that are informally classified as Tier I panels. Tier I panels are from well-respected manufacturers that have a good chance of being able to honor warranty claims. Tier I panels are understood to be of high quality, with predictable performance, durability, and content. Well over 80% (by weight) of the content of a PV panel is the tempered glass front and the aluminum frame, both of which are common building materials. Most of the remaining portion are common plastics, including polyethylene terephthalate in the backsheet, EVA encapsulation of the PV cells, polyphenyl ether in the junction box, and polyethylene insulation on the wire leads. The active, working components of the system are the silicon photovoltaic cells, the small electrical leads connecting them together, and to the wires coming out of the back of the panel. The electricity generating and conducting components makeup less than 5% of the weight of most panels. The PV cell itself is nearly 100% silicon, and silicon is the second most common element in the Earth's crust. The silicon for PV cells is obtained by high-temperature processing of quartz sand (SiO_2) that removes its oxygen molecules. The refined silicon is converted to a PV cell by adding extremely small amounts of boron and phosphorus, both of which are common and of very low toxicity.

The other minor components of the PV cell are also generally benign; however, some contain lead, which is a human toxicant that is particularly harmful to young children. The minor components include an extremely thin antireflective coating (silicon nitride or titanium dioxide), a thin layer of aluminum on the rear, and thin strips of silver alloy that are screen-printed on the front and rear of cell.[7] In order for the front and rear electrodes to make effective electrical contact with the proper layer of the PV cell, other materials (called glass frit) are mixed with the silver alloy and then heated to etch the metals into the cell. This glass frit historically contains a small amount of lead (Pb) in the form of lead oxide. The 60 or 72 PV cells in a PV panel are connected by soldering thin solder-covered copper tabs from the back of one cell to the front of the next cell. Traditionally a tin-based solder containing some lead (Pb) is used, but some manufacturers have switched to lead-free solder. The glass frit and/or the solder may contain trace amounts of other metals, potentially including some with human toxicity such as cadmium. However, testing to simulate the potential for leaching from broken panels, which is discussed in more detail below, did not find a potential toxicity threat from these trace elements. Therefore, the tiny amount of lead in the grass frit and the solder is the only part of silicon PV panels with a potential to create a negative health impact. However, as described below, the very limited amount of lead involved and its strong physical and chemical attachment to other components of the PV panel means that even in worst-case scenarios the health hazard it poses is insignificant.

As with many electronic industries, the solder in silicon PV panels has historically been a lead-based solder, often 36% lead, due to the superior properties of such solder. However, recent advances in lead-free solders have spurred a trend among PV panel manufacturers to reduce or remove the lead in their panels. According to the 2015 Solar Scorecard from the Silicon Valley Toxics Coalition, a group that tracks environmental responsibility of photovoltaic panel manufacturers, fourteen companies (increased from twelve companies in 2014) manufacture PV panels certified to meet the European Restriction of

Hazardous Substances (RoHS) standard. This means that the amount of cadmium and lead in the panels they manufacture fall below the RoHS thresholds, which are set by the European Union and serve as the world's de facto standard for hazardous substances in manufactured goods.[8] The Restriction of Hazardous Substances (RoHS) standard requires that the maximum concentration found in any homogenous material in a produce is less than 0.01% cadmium and less than 0.10% lead, therefore, any solder can be no more than 0.10% lead.[9]

While some manufacturers are producing PV panels that meet the RoHS standard, there is no requirement that they do so because the RoHS Directive explicitly states that the directive does not apply to photovoltaic panels.[10] The justification for this is provided in item 17 of the current RoHS Directive: "The development of renewable forms of energy is one of the Union's key objectives, and the contribution made by renewable energy sources to environmental and climate objectives is crucial. Directive 2009/28/EC of the European Parliament and of the Council of 23 April 2009 on the promotion of the use of energy from renewable sources (4) recalls that there should be coherence between those objectives and other Union environmental legislation. Consequently, this Directive should not prevent the development of renewable energy technologies that have no negative impact on health and the environment and that are sustainable and economically viable."

The use of lead is common in our modern economy. However, only about 0.5% of the annual lead consumption in the U.S. is for electronic solder for all uses; PV solder makes up only a tiny portion of this 0.5%. Close to 90% of lead consumption in the US is in batteries, which do not encapsulate the pounds of lead contained in each typical automotive battery. This puts the lead in batteries at great risk of leaching into the environment. Estimates for the lead in a single PV panel with lead-based solder range from 1.6 to 24 grams of lead, with 13g (less than half of an ounce) per panel seen most often in the literature.[11] At 13 g/panel[12], each panel contains one-half of the lead in a typical 12-gauge shotgun shell. This amount equates to roughly 1/750th of the lead in a single car battery. In a panel, it is all durably encapsulated from air or water for the full life of the panel.[14]

As indicated by their 20 to 30-year power warranty, PV modules are designed for a long service life, generally over 25 years. For a panel to comply with its 25-year power warranty, its internal components, including lead, must be sealed from any moisture. Otherwise, they would corrode and the panel's output would fall below power warranty levels. Thus, the lead in operating PV modules is not at risk of release to the environment during their service lifetime. In extreme experiments, researchers have shown that lead can leach from crushed or pulverized panels.[15, 16] However, more real-world tests designed to represent typical trash compaction that are used to classify waste as hazardous or non-hazardous show no danger from leaching.[17, 18] For more information about PV panel end-of-life, see the Panel Disposal section.

As illustrated throughout this section, silicon-based PV panels do not pose a material threat to public health and safety. The only aspect of the panels with potential toxicity concerns is the very small amount of lead in some panels. However, any lead in a panel is well sealed from environmental exposure for the operating lifetime of the solar panel and thus not at risk of release into the environment.

b. Cadmium Telluride (CdTe) PV Panels

This subsection examines the components of a cadmium telluride (CdTe) PV panel. Research demonstrates that they pose negligible toxicity risk to public health and safety while significantly reducing the public's exposure to cadmium by reducing coal emissions. As of mid-2016, a few hundred MWs of cadmium telluride (CdTe) panels, all manufactured by the U.S. company First Solar, have been installed in North Carolina.

Questions about the potential health and environmental impacts from the use of this PV technology are related to the concern that these panels contain cadmium, a toxic heavy metal. However, scientific studies have shown that cadmium telluride differs from cadmium due to its high chemical and thermal stability.[19] Research has shown that the tiny amount of cadmium in these panels does not pose a health or safety risk.[20] Further, there are very compelling reasons to welcome its adoption due to reductions in unhealthy pollution associated with burning coal. Every GWh of electricity generated by burning coal produces about 4 grams of cadmium air emissions.[21] Even though North Carolina produces a significant fraction of our electricity from coal, electricity from solar offsets much more natural gas than coal due to natural gas plants being able to adjust their rate of production more easily and quickly. If solar electricity offsets 90% natural gas and 10% coal, each 5-megawatt (5 MW_{AC}, which is generally 7 MW_{DC}) CdTe solar facility in North Carolina keeps about 157 grams, or about a third of a pound, of cadmium *out of* our environment.[22, 23]

Cadmium is toxic, but all the approximately 7 grams of cadmium in one CdTe panel is in the form of a chemical compound cadmium telluride, [24] which has 1/100th the toxicity of free cadmium.[25] Cadmium telluride is a very stable compound that is non-volatile and non-soluble in water. Even in the case of a fire, research shows that less than 0.1% of the cadmium is released when a CdTe panel is exposed to fire. The fire melts the glass and encapsulates over 99.9% of the cadmium in the molten glass.[27]

It is important to understand the source of the cadmium used to manufacture CdTe PV panels. The cadmium is a byproduct of zinc and lead refining. The element is collected from emissions and waste streams during the production of these metals and combined with tellurium to create the CdTe used in PV panels. If the cadmium were not collected for use in the PV panels or other products, it would otherwise either be stockpiled for future use, cemented and buried, or disposed of.[28] Nearly all the cadmium in old or broken panels can be recycled which can eventually serve as the primary source of cadmium for new PV panels.[29]

Similar to silicon-based PV panels, CdTe panels are constructed of a tempered glass front, one instead of two clear plastic encapsulation layers, and a rear heat strengthened glass backing (together >98% by weight). The final product is built to withstand exposure to the elements without significant damage for over 25 years. While not representative of damage that may occur in the field or even at a landfill, laboratory evidence has illustrated that when panels are ground into a fine powder, very acidic water is able to leach portions of the cadmium and tellurium,[30] similar to the process used to recycle CdTe panels. Like many silicon-based panels, CdTe panels are reported (as far back ask 1998[31]) to pass the EPA's Toxic Characteristic Leaching Procedure (TCLP) test, which tests the potential for crushed panels in a landfill to leach hazardous substances into groundwater.[32] Passing this test means that they are classified as non-hazardous waste and can be deposited in landfills.[33, 34] For more information about PV panel end-of-life, see the Panel Disposal section.

There is also concern of environmental impact resulting from potential catastrophic events involving CdTe PV panels. An analysis of worst-case scenarios for environmental impact from CdTe PV panels, including earthquakes, fires, and floods, was conducted by the University of Tokyo in 2013. After reviewing the extensive international body of research on CdTe PV technology, their report concluded, "Even in the worst-case scenarios, it is unlikely that the Cd concentrations in air and sea water will exceed the environmental regulation values."[35] In a worst-case scenario of damaged panels abandoned on the ground, insignificant amounts of cadmium will leach from the panels. This is because this scenario is much less conducive (larger module pieces, less acidity) to leaching than the conditions of the EPA's TCLP test used to simulate landfill conditions, which CdTe panels pass.[36]

First Solar, a U.S. company, and the only significant supplier of CdTe panels, has a robust panel take-back and recycling program that has been operating commercially since 2005.[37] The company states that it is "committed to providing a commercially attractive recycling solution for photovoltaic (PV) power plant and module owners to help them meet their module (end of life) EOL obligation simply, cost-effectively and responsibly." First Solar global recycling services to their customers to collect and recycle panels once they reach the end of productive life whether due to age or damage. These recycling service agreements are structured to be financially attractive to both First Solar and the solar panel owner. For First Solar, the contract provides the company with an affordable source of raw materials needed for new panels and presumably a diminished risk of undesired release of Cd. The contract also benefits the solar panel owner by allowing them to avoid tipping fees at a waste disposal site. The legal contract helps provide peace of mind by ensuring compliance by both parties when considering the continuing trend of rising disposal costs and increasing regulatory requirements.

c. CIS/CIGS and other PV technologies

Copper indium gallium selenide PV technology, often referred to as CIGS, is the second most common type of thin-film PV panel but a distant second behind CdTe. CIGS cells are composed of a thin layer of copper, indium, gallium, and selenium on a glass or plastic backing. None of these elements are very toxic, although selenium is a regulated metal under the Federal Resource Conservation and Recovery Act (RCRA).[38] The cells often also have an extremely thin layer of cadmium sulfide that contains a tiny amount of cadmium, which is toxic. The promise of high efficiency CIGS panels drove heavy investment in this technology in the past. However, researchers have struggled to transfer high efficiency success in the lab to low-cost full-scale panels in the field.[39] Recently, a CIGS manufacturer based in Japan, Solar Frontier, has achieved some market success with a rigid, glass-faced CIGS module that competes with silicon panels. Solar Frontier produces the majority of CIS panels on the market today.[40] Notably, these panels are RoHS compliant,[41] thus meeting the rigorous toxicity standard adopted by the European Union even thought this directive exempts PV panels. The authors are unaware of any completed or proposed utility-scale system in North Carolina using CIS/CIGS panels.

1.2.3 Panel End-of-Life Management

Concerns about the volume, disposal, toxicity, and recycling of PV panels are addressed in this subsection. To put the volume of PV waste into perspective, consider that by 2050, when PV systems installed in 2020 will reach the end of their lives, it is estimated that the global annual PV panel waste tonnage will be 10% of the 2014 global e-waste tonnage.[42] In the U.S., end-of-life disposal of solar products is governed by the Federal Resource Conservation and Recovery Act (RCRA), as well as state policies in some situations. RCRA separates waste into hazardous (not accepted at ordinary landfill) and solid waste (generally accepted at ordinary landfill) based on a series of rules. According to RCRA, the way to determine if a PV panel is classified as hazardous waste is the Toxic Characteristic Leaching Procedure (TCLP) test. This EPA test is designed to simulate landfill disposal and determine the risk of hazardous substances leaching out of the landfill.[43,44,45] Multiple sources report that most modern PV panels (both crystalline silicon and cadmium telluride) pass the TCLP test.[46,47] Some studies found that some older (1990s) crystalline silicon panels, and perhaps some newer crystalline silicon panels (specifics are not given about vintage of panels tested), do not pass the lead (Pb) leachate limits in the TCLP test.[48,49]

The test begins with the crushing of a panel into centimeter-sized pieces. The pieces are then mixed in an acid bath. After tumbling for eighteen hours, the fluid is tested for forty hazardous substances that all must be below specific threshold levels to pass the test. Research comparing TCLP conditions to conditions of damaged panels in the field found that simulated landfill conditions provide overly conservative estimates of leaching for field-damaged panels.[50] Additionally, research in Japan has found no detectable Cd leaching from cracked CdTe panels when exposed to simulated acid rain.[51]

Although modern panels can generally be landfilled, they can also be recycled. Even though recent waste volume has not been adequate to support significant PV-specific recycling infrastructure, the existing recycling industry in North Carolina reports that it recycles much of the current small volume of broken PV panels. In an informal survey conducted by the NC Clean Energy Technology Center survey in early 2016, seven of the eight large active North Carolina utility-scale solar developers surveyed reported that they send damaged panels back to the manufacturer and/or to a local recycler. Only one developer reported sending damaged panels to the landfill.

The developers reported at that time that they are usually paid a small amount per panel by local recycling firms. In early 2017, a PV developer reported that a local recycler was charging a small fee per panel to recycle damaged PV panels. The local recycling firm known to authors to accept PV panels described their current PV panel recycling practice as of early 2016 as removing the aluminum frame for local recycling and removing the wire leads for local copper recycling. The remainder of the panel is sent to a facility for processing the non-metallic portions of crushed vehicles, referred to as "fluff" in the recycling industry.[52] This processing within existing general recycling plants allows for significant material recovery of major components, including glass which is 80% of the module weight, but at lower yields than PV-specific recycling plants. Notably almost half of the material value in a PV panel is in the few grams of silver contained in almost every PV panel produced today. In the long-term, dedicated PV panel recycling plants can increase treatment capacities and maximize revenues resulting in better output quality and the ability to recover a greater fraction of the useful materials.[53] PV-specific panel recycling technologies have been researched and implemented to some extent for the past decade, and have been shown to be able to recover over 95% of PV material (semiconductor) and over 90% of the glass in a PV panel.[54]

A look at global PV recycling trends hints at the future possibilities of the practice in our country. Europe installed MW-scale volumes of PV years before the U.S. In 2007, a public-private partnership between the European Union and the solar industry set up a voluntary collection and recycling system called PV CYCLE. This arrangement was later made mandatory under the EU's WEEE directive, a program for waste electrical and electronic equipment.[55] Its member companies (PV panel producers) fully finance the association. This makes it possible for end-users to return the member companies' defective panels for recycling at any of the over 300 collection points around Europe without added costs. Additionally, PV CYCLE will pick up batches of 40 or more used panels at no cost to the user. This arrangement has been very successful, collecting and recycling over 13,000 tons by the end of 2015.[56]

In 2012, the WEEE Directive added the end-of-life collection and recycling of PV panels to its scope.[57] This directive is based on the principle of extended-producer-responsibility. It has a global impact because producers that want to sell into the EU market are legally responsible for end-of-life management. Starting in 2018, this directive targets that 85% of PV products "put in the market" in Europe are recovered and 80% is prepared for reuse and recycling.

The success of the PV panel collection and recycling practices in Europe provides promise for the future of recycling in the U.S. In mid-2016, the US Solar Energy Industry Association (SEIA) announced that they are starting a national solar panel recycling program with the guidance and support of many leading PV panel producers.[58] The program will aggregate the services offered by recycling vendors and PV manufacturers, which will make it easier for consumers to select a cost-effective and environmentally responsible end-of-life management solution for their PV products. According to SEIA, they are planning the program in an effort to make the entire industry landfill-free. In addition to the national recycling network program, the program will provide a portal for system owners and consumers with information on how to responsibly recycle their PV systems.

While a cautious approach toward the potential for negative environmental and/or health impacts from retired PV panels is fully warranted, this section has shown that the positive health impacts of reduced emissions from fossil fuel combustion from PV systems more than outweighs any potential risk. Testing shows that silicon and CdTe panels are both safe to dispose of in landfills, and are also safe in worst case conditions of abandonment or damage in a disaster. Additionally, analysis by local engineers has found that the current salvage value of the equipment in a utility scale PV facility generally exceeds general contractor estimates for the cost to remove the entire PV system.[59, 60, 61]

1.2.4 Non-Panel System Components (racking, wiring, inverter, transformer)

While previous toxicity subsections discussed PV panels, this subsection describes the non-panel components of utility-scale PV systems and investigates any potential public health and safety concerns. The most significant non-panel component of a ground-mounted PV system is the mounting structure of the rows of panels, commonly referred to as “racking”. The vertical post portion of the racking is galvanized steel and the remaining above-ground racking components are either galvanized steel or aluminum, which are both extremely common and benign building materials. The inverters that make the solar generated electricity ready to send to the grid have weather-proof steel enclosures that protect the working components from the elements. The only fluids that they might contain are associated with their cooling systems, which are not unlike the cooling system in a computer. Many inverters today are RoHS compliant.

The electrical transformers (to boost the inverter output voltage to the voltage of the utility connection point) do contain a liquid cooling oil. However, the fluid used for that function is either a non-toxic mineral oil or a biodegradable non-toxic vegetable oil, such as BIOTEMP from ABB. These vegetable transformer oils have the additional advantage of being much less flammable than traditional mineral oils. Significant health hazards are associated with old transformers containing cooling oil with toxic PCBs. Transfers with PCB-containing oil were common before PCBs were outlawed in the U.S. in 1979. PCBs still exist in older transformers in the field across the country.

Other than a few utility research sites, there are no batteries on- or off-site associated with utility-scale solar energy facilities in North Carolina, avoiding any potential health or safety concerns related to battery technologies. However, as battery technologies continue to improve and prices continue to decline we are likely to start seeing some batteries at solar facilities. Lithium ion batteries currently dominate the world utility-scale battery market, which are not very toxic. No non-panel system components were found to pose any health or environmental dangers.

1.4 Operations and Maintenance – Panel Washing and Vegetation Control

Throughout the eastern U.S., the climate provides frequent and heavy enough rain to keep panels adequately clean. This dependable weather pattern eliminates the need to wash the panels on a regular basis. Some system owners may choose to wash panels as often as once a year to increase production, but most in N.C. do not regularly wash any PV panels. Dirt build up over time may justify panel washing a few times over the panels' lifetime; however, nothing more than soap and water are required for this activity.

The maintenance of ground-mounted PV facilities requires that vegetation be kept low, both for aesthetics and to avoid shading of the PV panels. Several approaches are used to maintain vegetation at NC solar facilities, including planting of limited-height species, mowing, weed-eating, herbicides, and grazing livestock (sheep). The following descriptions of vegetation maintenance practices are based on interviews with several solar developers as well as with three maintenance firms that together are contracted to maintain well over 100 of the solar facilities in N.C. The majority of solar facilities in North Carolina maintain vegetation primarily by mowing. Each row of panels has a single row of supports, allowing sickle mowers to mow under the panels. The sites usually require mowing about once a month during the growing season. Some sites employ sheep to graze the site, which greatly reduces the human effort required to maintain the vegetation and produces high quality lamb meat.[62]

In addition to mowing and weed eating, solar facilities often use some herbicides. Solar facilities generally do not spray herbicides over the entire acreage; rather they apply them only in strategic locations such as at the base of the perimeter fence, around exterior vegetative buffer, on interior dirt roads, and near the panel support posts. Also unlike many row crop operations, solar facilities generally use only general use herbicides, which are available over the counter, as opposed to restricted use herbicides commonly used in commercial agriculture that require a special restricted use license. The herbicides used at solar facilities are primarily 2-4-D and glyphosate (Round-up®), which are two of the most common herbicides used in lawns, parks, and agriculture across the country. One maintenance firm that was interviewed sprays the grass with a class of herbicide known as a growth regulator in order to slow the growth of grass so that mowing is only required twice a year. Growth regulators are commonly used on highway roadsides and golf courses for the same purpose. A commercial pesticide applicator license is required for anyone other than the landowner to apply herbicides, which helps ensure that all applicators are adequately educated about proper herbicide use and application. The license must be renewed annually and requires passing of a certification exam appropriate to the area in which the applicator wishes to work. Based on the limited data available, it appears that solar facilities in N.C. generally use significantly less herbicides per acre than most commercial agriculture or lawn maintenance services.

2. Electromagnetic Fields (EMF)

PV systems do not emit any material during their operation; however, they do generate electromagnetic fields (EMF), sometimes referred to as radiation. EMF produced by electricity is non-ionizing radiation, meaning the radiation has enough energy to move atoms in a molecule around (experienced as heat), but not enough energy to remove electrons from an atom or molecule (ionize) or to damage DNA. As shown below, modern humans are all exposed to EMF throughout our daily lives without negative health impact. Someone outside of the fenced perimeter of a solar facility is not exposed to significant EMF from the solar facility. Therefore, there is no negative health impact from the EMF produced in a solar farm. The following paragraphs provide some additional background and detail to support this conclusion.

Since the 1970s, some have expressed concern over potential health consequences of EMF from electricity, but no studies have ever shown this EMF to cause health problems.[63] These concerns are based on some epidemiological studies that found a slight increase in childhood leukemia associated with average exposure to residential power-frequency magnetic fields above 0.3 to 0.4 µT (microteslas) (equal to 3.0 to 4.0 mG (milligauss)). µT and mG are both units used to measure magnetic field strength. For comparison, the average exposure for people in the U.S. is one mG or 0.1 µT, with about 1% of the population with an average exposure in excess of 0.4 µT (or 4 mG).[64] These epidemiological studies, which found an association but not a causal relationship, led the World Health Organization's International Agency for Research on Cancer (IARC) to classify ELF magnetic fields as "possibly carcinogenic to humans". Coffee also has this classification. This classification means there is limited evidence but not enough evidence to designate as either a "probable carcinogen" or "human carcinogen". Overall, there is very little concern that ELF EMF damages public health. The only concern that does exist is for long-term exposure above 0.4 µT (4 mG) that may have some connection to increased cases of childhood leukemia. In 1997, the National Academies of Science were directed by Congress to examine this concern and concluded:

> "Based on a comprehensive evaluation of published studies relating to the effects of power-frequency electric and magnetic fields on cells, tissues, and organisms (including humans), the conclusion of the committee is that the current body of evidence does not show that exposure to these fields presents a human-health hazard. Specifically, no conclusive and consistent evidence shows that exposures to residential electric and magnetic fields produce cancer, adverse neurobehavioral effects, or reproductive and developmental effects."[65]

There are two aspects to electromagnetic fields, an electric field and a magnetic field. The electric field is generated by voltage and the magnetic field is generated by electric current, i.e., moving electrons. A task group of scientific experts convened by the World Health Organization (WHO) in 2005 concluded that there were no substantive health issues related to *electric* fields (0 to 100,000 Hz) at levels generally encountered by members of the public.[66] The relatively low voltages in a solar facility and the fact that electric fields are easily shielded (i.e., blocked) by common materials, such as plastic, metal, or soil means that there is no concern of negative health impacts from the electric fields generated by a solar facility. Thus, the remainder of this section addresses magnetic fields. Magnetic fields are not shielded by most common materials and thus can easily pass through them. Both types of fields are strongest close to the source of electric generation and weaken quickly with distance from the source.

The direct current (DC) electricity produced by PV panels produce stationary (0 Hz) electric and magnetic fields. Because of minimal concern about potential risks of stationary fields, little scientific research has examined stationary fields' impact on human health.[67] In even the largest PV facilities, the DC voltages and currents are not very high. One can illustrate the weakness of the EMF generated by a PV panel by placing a compass on an operating solar panel and observing that the needle still points north.

While the electricity throughout the majority of a solar site is DC electricity, the inverters convert this DC electricity to alternating current (AC) electricity matching the 60 Hz frequency of the grid. Therefore, the inverters and the wires delivering this power to the grid are producing non-stationary EMF, known as extremely low frequency (ELF) EMF, normally oscillating with a frequency of 60 Hz. This frequency is at the low-energy end of the electromagnetic spectrum. Therefore, it has less energy than other commonly encountered types of non-ionizing radiation like radio waves, infrared radiation, and visible light.

The wide use of electricity results in background levels of ELF EMFs in nearly all locations where people spend time – homes, workplaces, schools, cars, the supermarket, etc. A person's average exposure depends upon the sources they encounter, how close they are to them, and the amount of time they spend there.[68] As stated above, the average exposure to magnetic fields in the U.S. is estimated to be around one mG or 0.1 µT, but can vary considerably depending on a person's exposure to EMF from electrical devices and wiring.[69] At times we are often exposed to much higher ELF magnetic fields, for example when standing three feet from a refrigerator the ELF magnetic field is 6 mG and when standing three feet from a microwave oven the field is about 50 mG.[70] The strength of these fields diminish quickly with distance from the source, but when surrounded by electricity in our homes and other buildings moving away from one source moves you closer to another. However, unless you are inside of the fence at a utility-scale solar facility or electrical substation it is impossible to get very close to the EMF sources. Because of this, EMF levels at the fence of electrical substations containing high voltages and currents are considered "generally negligible".[71, 72]

The strength of ELF-EMF present at the perimeter of a solar facility or near a PV system in a commercial or residential building is significantly lower than the typical American's average EMF exposure.[73, 74] Researchers in Massachusetts measured magnetic fields at PV projects and found the magnetic fields dropped to very low levels of 0.5 mG or less, and in many cases to less than background levels (0.2 mG), at distances of no more than nine feet from the residential inverters and 150 feet from the utility-scale inverters.[75] Even when measured within a few feet of the utility-scale inverter, the ELF magnetic fields were well below the International Commission on Non-Ionizing Radiation Protection's recommended magnetic field level exposure limit for the general public of 2,000 mG.[76] It is typical that utility scale designs locate large inverters central to the PV panels that feed them because this minimizes the length of wire required and shields neighbors from the sound of the inverter's cooling fans. Thus, it is rare for a large PV inverter to be within 150 feet of the project's security fence.

Anyone relying on a medical device such as pacemaker or other implanted device to maintain proper heart rhythm may have concern about the potential for a solar project to interfere with the operation of his or her device. However, there is no reason for concern because the EMF outside of the solar facility's fence is less than 1/1000 of the level at which manufacturers test for ELF EMF interference, which is 1,000 mG.[77] Manufacturers of potentially affected implanted devices often provide advice on electromagnetic interference that includes avoiding letting the implanted device get too close to certain sources of fields such as some household appliances, some walkie-talkies, and similar transmitting devices. Some manufacturers' literature does not mention high-voltage power lines, some say that exposure in public areas should not give interference, and some advise not spending extended periods of time close to power lines.[78]

3. Electric Shock and Arc Flash Hazards

There is a real danger of electric shock to anyone entering any of the electrical cabinets such as combiner boxes, disconnect switches, inverters, or transformers; or otherwise coming in contact with voltages over 50 Volts.[79] Another electrical hazard is an arc flash, which is an explosion of energy that can occur in a short circuit situation. This explosive release of energy causes a flash of heat and a shockwave, both of which can cause serious injury or death. Properly trained and equipped technicians and electricians know how to safely install, test, and repair PV systems, but there is always some risk of injury when hazardous voltages and/or currents are present. Untrained individuals should not attempt to inspect, test, or repair any aspect of a PV system due to the potential for injury or death due to electric shock and arc flash, The National Electric Code (NEC) requires appropriate levels of warning signs on all electrical components based on the level of danger determined by the voltages and current potentials. The national electric code also requires the site to be secured from unauthorized visitors with either a six-foot chain link fence with three strands of barbed wire or an eight-foot fence, both with adequate hazard warning signs.

4. Fire Safety

The possibility of fires resulting from or intensified by PV systems may trigger concern among the general public as well as among firefighters. However, concern over solar fire hazards should be limited because only a small portion of materials in the panels are flammable, and those components cannot self-support a significant fire. Flammable components of PV panels include the thin layers of polymer encapsulates surrounding the PV cells, polymer backsheets (framed panels only), plastic junction boxes on rear of panel, and insulation on wiring. The rest of the panel is composed of non-flammable components, notably including one or two layers of protective glass that make up over three quarters of the panel's weight.

Heat from a small flame is not adequate to ignite a PV panel, but heat from a more intense fire or energy from an electrical fault can ignite a PV panel.[80] One real-world example of this occurred during July 2015 in an arid area of California. Three acres of grass under a thin film PV facility burned without igniting the panels mounted on fixed-tilt racks just above the grass.[81] While it is possible for electrical faults in PV systems on homes or commercial buildings to start a fire, this is extremely rare.[82] Improving understanding of the PV-specific risks, safer system designs, and updated fire-related codes and standards will continue to reduce the risk of fire caused by PV systems.

PV systems on buildings can affect firefighters in two primary ways, 1) impact their methods of fighting the fire, and 2) pose safety hazard to the firefighters. One of the most important techniques that firefighters use to suppress fire is ventilation of a building's roof. This technique allows superheated toxic gases to quickly exit the building. By doing so, the firefighters gain easier and safer access to the building, Ventilation of the roof also makes the challenge of putting out the fire easier. However, the placement of rooftop PV panels may interfere with ventilating the roof by limiting access to desired venting locations.

New solar-specific building code requirements are working to minimize these concerns. Also, the latest National Electric Code has added requirements that make it easier for first responders to safely and effectively turn off a PV system. Concern for firefighting a building with PV can be reduced with proper fire fighter training, system design, and installation. Numerous organizations have studied fire fighter safety related to PV. Many organizations have published valuable guides and training programs. Some notable examples are listed below.

- The International Association of Fire Fighters (IAFF) and International Renewable Energy Council (IREC) partnered to create an online training course that is far beyond the PowerPoint click-and-view model. The self-paced online course, "Solar PV Safety for Fire Fighters," features rich video content and simulated environments so fire fighters can practice the knowledge they've learned. www.iaff.org/pvsafetytraining
- Photovoltaic Systems and the Fire Code: Office of NC Fire Marshal
- Fire Service Training, Underwriter's Laboratory

- Firefighter Safety and Response for Solar Power Systems, National Fire Protection Research Foundation
- Bridging the Gap: Fire Safety & Green Buildings, National Association of State Fire Marshalls
- Guidelines for Fire Safety Elements of Solar Photovoltaic Systems, Orange County Fire Chiefs Association
- Solar Photovoltaic Installation Guidelines, California Department of Forestry & Fire Protection, Office of the State Fire Marshall
- PV Safety & Firefighting, Matthew Paiss, Homepower Magazine
- PV Safety and Code Development: Matthew Paiss, Cooperative Research Network

Summary

The purpose of this paper is to address and alleviate concerns of public health and safety for utility-scale solar PV projects. Concerns of public health and safety were divided and discussed in the four following sections: (1) Toxicity, (2) Electromagnetic Fields, (3) Electric Shock and Arc Flash, and (4) Fire. In each of these sections, the negative health and safety impacts of utility-scale PV development were shown to be negligible, while the public health and safety benefits of installing these facilities are significant and far outweigh any negative impacts.

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CdTe PV: Real and Perceived EHS Risks

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ABSTRACT

As CdTe photovoltaics reached commercialization, questions were raised about potential cadmium emissions from CdTe PV modules. Some have attacked the CdTe PV technology as unavoidably polluting the environment, and made comparisons of hypothetical emissions from PV modules to cadmium emissions from coal-fired power plants. This paper gives an overview of the technical issues pertinent to these questions and further explores the potential of environmental, health, and safety (EHS) risks during production, use, and decommissioning of CdTe PV modules. The following issues are discussed: (a) the physical and toxicological properties of CdTe, (b) comparisons of Cd use in CdTe PV with its use in other technologies and products, and (c) the possibility of CdTe releases from PV modules.

1. Toxicology of CdTe

Elemental cadmium, which forms CdTe when reacted with tellurium (Te), is a lung carcinogen, and long-term exposures can cause detrimental effects on kidney and bone. Very limited data exist on CdTe toxicology, and no comparisons with the element Cd have been made [1]. However, CdTe is a more stable and less soluble compound than Cd and, therefore, is probably less toxic than Cd. However, OSHA groups all Cd compounds together, and as a general guidance, all facilities working with any such compounds should control the indoor concentrations of CdTe dust or fumes to below the Permissible Exposure Level-Time Weighted Average (PEL-TWA) Cd concentration of 0.005 mg/m^3.

The U.S. CdTe PV industry is vigilant in preventing health risks and has established proactive programs in industrial hygiene and environmental control. Workers' exposure to cadmium compounds in PV manufacturing facilities is controlled by rigorous industrial hygiene practices and is monitored by frequent medical tests. Results of years of biomonitoring have shown that there are no significant observed increases in levels of worker exposure [2].

2. Amount of Cd Compounds Encapsulated in CdTe Modules and NiCd Batteries

The amount of Cd compounds in PV modules is proportional to the area of the module and the thickness of the CdTe and CdS layers. Most CdTe layers are about 1-3 microns thick, and most CdS layers are about 0.2 microns thick. Therefore, about 3–9 g/m^2 Cd is contained in CdTe, and less than 1 g/m^2 is contained in CdS. A reasonable average amount would be about 7 g/m^2 Cd in CdTe modules. Layer thickness is expected to be reduced as research and development efforts continue, further reducing the amount of Cd compounds in the cells [3].

A CdTe module of 10% sunlight-to-electricity conversion efficiency produces about 100 W of output under standard sunlight conditions. So, there is an average of 7 g/100 W = 70 g per kW of electric power produced. In an average solar location in the United States, such as Kansas, a one-square-meter, 10%-efficient CdTe module containing 7 g of Cd would produce about 5400 kWh over its expected service life of 30 years. That is about 770 kWh per gram of Cd, or 0.001 g/kWh. (Note, this amount is in the module and is <u>not</u> an emission. It can be completely recycled.)

Table 1 shows a comparison of the Cd content in CdTe PV and in NiCd batteries. CdTe modules occupying 1 m^2 contain less Cd than one C–size flashlight battery. A 1-kW system would contain as much Cd as seven C-size batteries. On a per kWh basis, assuming that a NiCd battery can be recharged 700 to 1200 times over its life [4], it would produce an average of 0.046 kWh per g of its weight, which corresponds to 0.306 kWh per g of Cd contained in the battery. This is 2,500 times less than a CdTe PV module. Thus the value of using Cd in PV is much greater than its value elsewhere in the marketplace.

Table 1. Cd Content in CdTe PV and NiCd Batteries

	g/unit	g/kW (ton/GW)	mg/kWh (kg/GWh)
PV CdTe	7 g/m2	70	1.3
NiCd battery -C size	10		3265.

3. EHS Risks during Cadmium Mining

CdTe is manufactured from pure Cd and Te, both of which are by-products of smelting prime metals (e.g., Cu, Zn, Pb, and Au). About 80% of the world's production of cadmium is generated as a by-product of smelting zinc ores. Its major feedstock, sphalerite (ZnS), contains about 0.25% Cd. Secondary cadmium is produced from recycling spent NiCd batteries and other scrap. The demand of zinc has been steadily increasing for decades as driven by economic growth. Therefore, cadmium (in impure form) is produced regardless of its use. Cadmium is used primarily (~65%) in nickel-cadmium rechargeable batteries, paint pigments (~17%), plastic stabilizers (~10%), metal plating (~5%), and metal solders (~2%). When there is no cost-effective market for the metal, raw Cd is disposed of [5].

The total Cd use in the United States was 2,600 tons in 1997; globally, the total use is 19,000 to 20,000 tons. Using only 3% of the U.S. consumption of cadmium (i.e., 78 tons) in the manufacture of CdTe solar cells would generate over 1 GW of new PV per year. Note that the total current PV capacity in the United States is only 0.3 GW and is projected to grow (under optimistic assumptions) to about 3.2 GW/yr by 2020. Even if we envision PV production that is an order of magnitude higher, it would require only about a third of the current U.S. Cd consumption. Yet to change the world's energy infrastructure with CdTe PV, much less Cd would be needed, and it would not impact the overall smelting of Cd at all. In fact, it would provide a beneficial use of Cd that could otherwise be cemented or end up in a waste dump.

4. EHS Risks in CdTe PV Manufacture

In production facilities, workers may be exposed to Cd compounds through the air if contaminated, and by ingestion from hand-to-mouth contact. Inhalation is probably the most important pathway, because of the larger potential for exposure and higher absorption efficiency of Cd compounds through the lung than through the gastrointestinal tract. Processes in which Cd compounds are used or produced in the form of fine particulates or vapor present larger hazards to health. Hazards to workers may arise from feedstock preparation, fume/vapor leaks, etching of excess materials from panels, maintenance operations (e.g., scraping and cleaning), and during waste handling. Caution must be exercised when working with this material, and several layers of control must be implemented to prevent exposure of the employees. In general, the hierarchy of controls includes engineering controls, personal protective equipment, and work practices. The U.S. industry is vigilant in preventing health risks, and has established proactive programs in industrial hygiene and environmental control. Workers' exposure to cadmium in PV manufacturing facilities is controlled by rigorous industrial hygiene practices and is continuously monitored by medical tests, thus preventing health risks [2].

5. Can CdTe from PV Modules Harm Our Health or the Environment?

Toxic compounds cannot cause any adverse health effects unless they enter the human body in harmful doses. The only pathways by which people might be exposed to PV compounds from a finished module are by accidentally ingesting flakes or dust particles, or inhaling dust and fumes. The thin CdTe/CdS layers are stable and solid and are encapsulated between thick layers of glass. Unless the module is purposely ground to a fine dust, dust particles cannot be generated. The vapor pressure of CdTe at ambient conditions is zero. Therefore, it is impossible for any vapors or dust to be generated when using PV modules.

The only issue of some concern is the disposal of the well-encapsulated, relatively immobile CdTe at the end of the modules' useful life. Thin CdTe PV end-of-life or broken modules pass Federal (TCLP-RCRA) leaching criteria for non-hazardous waste [6]. Therefore, according to current laws, such modules could be disposed of in landfills. However, recycling PV modules offers an important marketing advantage, and the industry is considering it as they move toward large and cost-effective production [7,8]. This issue of recycling is not unique to CdTe. The disposal of current x-Si modules, most of which incorporate Pb-based solder, presents similar concerns. Recycling the modules at the end of their useful life completely resolves any environmental concerns.

6. Do CdTe Modules Present Additional Health Risks during a Fire?

The flame temperatures in typical U.S. residential fires are not high enough to vaporize CdTe; flame temperatures in roof fires are in the 800°–900°C range, and, in basement rooms, in the 900°–1000°C range [9]. The melting point of CdTe is 1041°C, and evaporation starts at 1050 °C. Sublimation occurs at lower temperatures, but the vapor pressure of CdTe at 800 °C is only 2.5 torr (0.003 atm). The melting point of CdS is 1750°C, and its vapor pressure due to sublimation is only 0.1 torr at 800°C. Preliminary studies at Brookhaven [10] and at the GSF Institute of Chemical Ecology in Germany [11] showed that CdTe releases are unlikely to occur during residential fires or during accidental breakage. The thin layers of CdTe and CdS are sandwiched between glass plates; at typical flame temperatures (800°–1000°C), these compounds would be encapsulated inside the molten glass so that any Cd vapor emissions would be unlikely. In any case, the fire itself and other sources of emissions within the burning structure are expected to pose an incomparably greater hazard than any potential Cd emissions from PV systems.

7. CdTe PV Can Prevent Cd Emissions from Coal-Burning Power Plants

Coal-burning routinely generates Cd, because Cd is contained in the coal. A typical U.S. coal-power plant will generate waste in the form of fine dust or cake, containing about 140 g of Cd, for every GWh of electricity produced. In addition, a minimum of 2 g of Cd will be emitted from the stack (for plants with perfectly maintained electrostatic precipitators or bag-houses operating at 98.6% efficiency, and median concentration of Cd in U.S. coal of 0.5 ppm) [12]. Power plants with less efficient pollution controls will produce more Cd in gaseous form. Furthermore, a typical U.S. coal-power plant emits about 1000 tons of CO_2, 8 tons of SO_2, 3 tons of NOx, and 0.4 tons of particulates per GWh of electricity produced. All these emissions will be avoided when PV replaces coal-burning for some fraction of electricity generation.

8. Conclusion

The potential EHS risks related to the cadmium content of CdTe PV modules were highlighted for all the different phases of a large-scale implementation of the technology. The basic conclusions are:

Cd Mining: Cadmium is produced primarily as a by-product of zinc production. Because Zn is produced in large quantities, substantial quantities of cadmium is generated as a by-product, no matter how much Cd is used in PV, and can either be put to *beneficial* uses or *discharged* into the environment. When the market does not absorb the Cd generated by metal smelters/refiners, it is cemented and buried, stored for future use, or disposed of to landfills as hazardous waste. Arguably, encapsulating cadmium as CdTe in PV modules presents a safer use than its current uses and is much preferred to disposing it off.

CdTe PV Manufacture: In CdTe PV production facilities, workers may be exposed to Cd compounds through the air they breathe and by ingestion from hand-to-mouth contact. These are real risks and continuing vigilance is required. However, current industrial practice suggests that these risks can be managed and controlled successfully.

CdTe PV Use: No emissions of any kind can be generated when using PV modules under normal conditions. Any comparisons made with cadmium emissions from coal fired power plants are erroneous, because they compare potential accidental emissions from PV systems to routine (unavoidable) emissions from modern coal-fired plants. In reality, PV, when it replaces coal-burning for electricity generation, will prevent Cd emissions in addition to preventing large quantities of CO_2, SO_2, NOx, and particulate emissions.

Related to NiCd batteries, a CdTe PV module uses Cd about 2500 times more efficiently in producing electricity. A 1-kW CdTe PV system contains as little cadmium as seven size-C NiCd batteries. Thus the incremental risk to the house occupants or firefighters from roof fires is negligible. In addition, it is unlikely that CdTe will vaporize during residential fires because the flames are not hot enough. In any case, the fire itself would pose a much greater hazard than any potential Cd emissions from PV systems.

CdTe PV Decommissioning: The only environmental issue is what to do with the modules about 30 years later, if they are no longer useful. Although cadmium telluride is encapsulated between sheets of glass and is unlikely to leach out, the PV industry is considering recycling of these modules at the end of their useful life. Recycling will completely resolve any environmental concerns.

In conclusion, the environmental risks from CdTe PV are minimal. Every energy source or product may present some environmental, health, and safety hazards, and those of CdTe are by no means barriers to scaling-up the technology.

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13. ABSTRACT *(Maximum 200 words)* As CdTe photovoltaics reached commercialization, questions have been raised about potential cadmium emissions from CdTe PV modules. Some have attacked the CdTe PV technology as unavoidably polluting the environment, and made comparisons of hypothetical emissions from PV modules to cadmium emissions from coal fired power plants. This paper gives an overview of the technical issues pertinent to these questions and further explores the potential of EHS risks during production, use and decommissioning of CdTe PV modules. The following issues are discussed: (a) The physical and toxicological properties of CdTe, (b) comparisons of Cd use in CdTe PV with its use in other technologies and products, and the (c) the possibility of CdTe releases from PV modules.			
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Broader Perspectives

Emissions and Encapsulation of Cadmium in CdTe PV Modules During Fires‡

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Fires in residential and commercial properties are not uncommon. If such fires involve the roof, photovoltaic arrays mounted on the roof will be exposed to the flames. The amount of cadmium that can be released in fires involving CdTe PV and the magnitude of associated health risks has been debated. The current study aims in delineating this issue. Previous thermogravimetric studies of CdTe, involved pure CdTe and single-glass PV modules. The current study is based on glass–glass CdTe PV modules which are the only ones in the market. Pieces of commercial CdTe photovoltaic (PV) modules, sizes 25 × 3 cm, were heated to temperatures up to 1100°C to simulate exposure to residential and commercial building fires. The temperature rate and duration in these experiments were defined according to standard protocols. Four different types of analysis were performed to investigate emissions and redistribution of elements in the matrix of heated CdTe PV modules: (1) measurements of sample weight loss as a function of temperature; (2) analyses of Cd and Te in the gaseous emissions; (3) Cd distribution in the heated glass using synchrotron X-ray fluorescence microprobe analysis; and (4) chemical analysis for Cd and Te in the acid-digested glass. These experiments showed that almost all (i.e., 99·5%) of the cadmium content of CdTe PV modules was encapsulated in the molten glass matrix; a small amount of Cd escaped from the perimeter of the samples before the two sheets of glass melted together. Adjusting for this loss in full-size modules, results in 99·96% retention of Cd. Multiplying this with the probability of occurrence for residential fires in wood-frame houses in the US (e.g., 10^{-4}), results in emissions of 0·06 mg/GWh; the probability of sustained fires and subsequent emissions in adequately designed and maintained utility systems appears to be zero. Published in 2005 by John Wiley & Sons, Ltd.

KEY WORDS: CdTe; photovoltaics; LCA; life-cycle assessment; fire emissions; cadmium; leaching; ion-exchange

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1. INTRODUCTION

In the United States, about 1 in 10 000 wood-frame houses may catch fire during the year. If such fires involve the roof, photovoltaic arrays that are mounted there would be exposed to the flames. There are no studies in the literature regarding fire effects on a utility scale PV system, and we are not aware of a reported fire in any utility PV system. Tucson Electric in Arizona, US, has experienced two cases of incorrect wiring that each caused melting of a glass module, and also three cases of small fires in metal DC terminal boxes due to bad connections, but none of these incidents caused a fire to the rest of the field. In addition there were six documented lighting strikes on PV arrays, none of which resulted in a fire. Overall, due to the lack of combustible materials, the risk of a fire that could consume a utility array is extremely small. There is a risk of fire from external fuel sources (e.g., grass/bush fires), but this is controlled through design and operational practices (e.g., metal enclosures of potential ignition sources, firebreaks, controlling vegetation, limited access). Therefore, our study was designed to simulate the potential of toxic emissions only from roof-mounted photovoltaic arrays.

Previous thermogravimetric studies of CdTe at the GSF Institute of Chemical Ecology in Munich, Germany, involved pure CdTe and a small number of tests on single glass PV modules.[1,2] The pure CdTe tests showed a small weight increase between 570 and 800°C, possibly due to oxidation. The oxidized product remained stable until about 1050°C, above which the compound began to vaporize.[2] Other experiments at non-oxidizing conditions (Ar atmosphere), showed a high loss of CdTe in the 900–1050°C range. No experiments involving CdTe encapsulated between two sheets of glass are reported.

The current study is based on glass–CdTe–glass PV modules, which are the only ones in the market. (Single-glass panels are not considered by any manufacturer at this time). Pieces of commercial CdTe photovoltaic (PV) modules, approximately 25 × 3 cm, were heated to temperatures up to about 1100°C to simulate exposure to residential fires. The heating rate and duration in these experiments were defined according to standard Underwriters Laboratories (UL)[3] and American Society for Testing and Materials (ASTM)[4] test protocols. The total mass loss was calculated by weight measurements. The amounts of Cd and Te releases to the atmosphere were calculated by capturing these elements in solutions of nitric acid or hydrochloric acid and hydrogen peroxide. Also, the distribution of Cd in the burnt pieces was measured with synchrotron X-ray microprobe analysis.

2. CdTe PV MODULE THERMAL CHARACTERISTICS

The composition of the tested samples is shown in Table I. These samples were cut from standard commercial modules produced by First Solar Inc. of Toledo, Ohio. The frames, rails and wires were not included in the experiments. The concentration of the metals was determined by grinding a control piece and leaching in acid/oxidizer solution; these were also cross-referenced with mass balance calculations at the manufacturing plant scale. The concentrations of the glass and ethylene vinyl acetate (EVA) are based on weight measurements.

Table I. Composition of samples

Compound	wt (%)
Total glass	96·061
EVA	2·614
Total Cd	0·059*
Total Te	0·063*
Total Cu	0·011*
Other	1·192

*The uncertainty of these measurements is 5% as determined by ICP analysis.

Table II. CdTe vapor pressure coefficients for equation (2)

A	*B*	*T* (K)	Reference
−9500	6·427	731–922	7
−11 493	7·99	1085–1324	8
−9764	6·572	773–1010	9
−10 000	6·823	1053–1212	10

The EVA is expected to either burn or decompose at approximately 450°C according to experiments involving EVA and back surface sheet on crystalline Si cells.[5]

The module's substrate and front cover are sheets of glass, which has a softening point of 715°C. The following compounds are present or can be formed during the heating (CdTe, CdS, CdO, TeO_2, TeO_4, $CdCl_2$ and $CuCl_2$); other oxides may also be formed. Some of these compounds produce vapors by sublimation at temperatures below their melting points.

The sublimation of pure CdTe is described by the reaction:[6]

$$\mathrm{CdTe(s)} = \mathrm{Cd(g)} + 0{\cdot}5\mathrm{Te_2(g)} \tag{1}$$

The vapor pressure due to sublimation of CdTe is estimated by the Antoine equation:

$$\log P(\mathrm{atm}) = AT^{-1} + B \tag{2}$$

Values for the coefficients *A* and *B* are shown in Table II.

As shown by the CdTe curves in Figure 1, these four sets of coefficients give approximately the same vapor pressure estimates.

The vapor pressure of pure CdS and TeO_2 can be estimated by the following equation[11,12]

$$\log P(\mathrm{mm\ Hg}) = A + BT^{-1} + C\log T + DT + ET^2 \tag{3}$$

where the constants *A*, *B*, *C*, *D* and *E* are listed in Table III.

As shown in Figure 1, CdS has the lowest vapor pressure of the considered pure cadmium compounds. The vapor pressure of CdTe is two orders of magnitude lower than that of $CdCl_2$ in the temperature range of our experiments. The CdTe pressure due to sublimation at 800°C is about 2·4 torr.

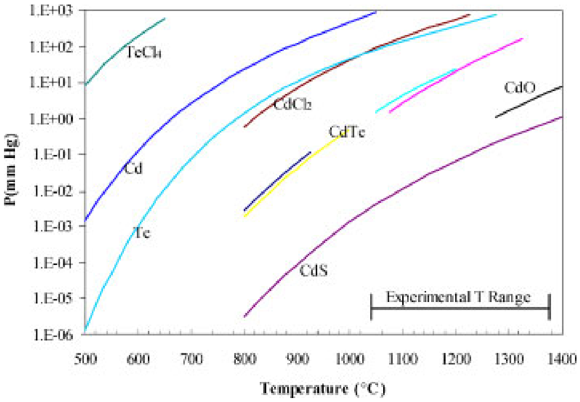

Figure 1. Vapor pressure of cadmium compounds

Table III. Vapor pressure coefficients for equation (3)

Component	*A*	*B*	*C*	*D*	*E*	*T*(K)
CdS(s)	16·06	−11 460	−2·5	—	—	298–1203
$CdCl_2$(s)	17·46	−9270	−2·11	—	—	298–840
$CdCl_2$(l)	25·907	−9183	−5·04	—	—	840–1233
CdO(s)	42·8498	−1 5 443	−10·651	$2{\cdot}0645 \times 10^{-3}$	$-1{\cdot}704 \times 10^{-7}$	1273–1832
TeO_2(s)	23·51	−13 940	−3·52	—	—	298–10 006
$TeCl_4$	225·5681	−13 194	−80·8999	$4{\cdot}5316 \times 10^{-2}$	$-1{\cdot}044 \times 10^{-5}$	506–665

3. THERMOGRAVIMETRIC TESTS

Typical flame temperatures in residential fires are in the 800–900°C range for roof fires and 900–1000°C in fires involving the whole house as measured in basement rooms.[13] In this study we extended this range to the limit of our heating apparatus, which was 1100°C.

3.1. Protocol

There are several validated fire test methods used by the industry and the government in evaluating flammability and fire resistance of materials. Two test methods which are applicable to our task are the Underwriters Laboratories Inc., UL Standard 1256 for Fire Test of Roof Deck Constructions,[3] and the American Society for Testing and Materials (ASTM) Standard E119-98 for Fire Tests of Building Construction and Materials.[4] The later is also adopted by the Uniform Building Code as UBC Standard 7-1. The UL 1256 Standard involves direct fire heating at 760°C, for 30 min. The ASTM Standard involves gradual heating controlled to conform to the standard time–temperature curve shown in Figure 2. Our tests were done in a tube furnace where we adjusted the heating rate to exactly follow this standard temperature rate curve. Pieces of commercial CdTe photovoltaic (PV) modules, nominally 25 × 3 cm were used. The furnace was heated by electrical resistance and contained three zones, so uniformity of the central heated zone was accomplished. The pieces of PV module were placed on alumina plates and were positioned inside a quartz tube in the central uniform-temperature zone of the oven. The tube was fitted with an inlet and outlet for gas flow and was sealed from the outside atmosphere. Air was introduced into the furnace at a rate of 10 l/min, producing a linear velocity of 0·04 m/s above the sample. The airflow carried any released vapor/aerosols from the PV sample to the outlet. The effluent flow was passed through a glass-wool filter and two bubbler-scrubbers in series containing a 0·01 M nitric acid solution in order to capture the Cd and Te releases from the PV module. The quartz tube and glass-wool were leached for 24 h in nitric acid. Complete removal of the metals from the glass-wool filters was verified by additional leaching using hydrochloric acid and hydrogen peroxide solutions for 48 h in a tumbling machine.

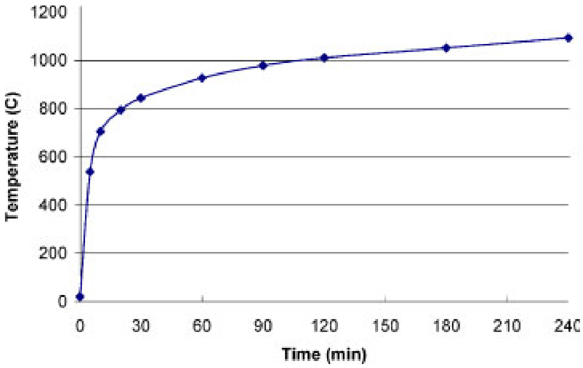

Figure 2. Temperature and heating duration for each experiment (as per ASTM E119-98 Standard)

Table IV. Measured loss of mass

			Cd emissions		Te emissions	
Test	*T* (°C)	Weight loss (% sample)	(g/m^2)	(% of Cd content)	(g/m^2)	(% of Te content)
1	760	1·9	0·056	0·6	0·046	0·4
2	900	2·1	0·033	0·4	0·141	1·2
3	1000	1·9	0·048	0·5	1·334	11·6
4	1100	2·2	0·037	0·4	2·680	22·5

3.2. Results

The PV samples were weighed before and after each experiment. Weight loss in the range of 1·9–2·2% of the total weight was recorded (Table IV). Observations of black residues in the reactor walls and filters indicate that most of this weight loss was caused by the decomposition and vaporization of EVA.

The acidic solutions from rinsing of the reactor walls, rinsing of the glass-wool filters in the reactor exhaust, and the scrubber liquids, were analyzed for Cd and Te by inductively coupled plasma (ICP) optical emission spectroscopy (Varian Liberty 100). A small loss of Cd amounting to 0·4–0·6% of the total Cd in the sample was recorded (Table IV). The loss of Te was also very small during heating at 760 and 900°C, but it increased significantly at higher temperatures.

Measurements of the total mass of Cd and Te in the untreated sample were obtained by breaking the sample and leaching the metal content in a tumbling machine with a solution of sulfuric acid and hydrogen peroxide. Complete leaching of the metals was verified by leaching with hydrochloric acid/H_2O_2 solutions. The uncertainty of the ICP analysis was determined with frequent calibration to be $\leq 5\%$.

4. MICROBEAM X-RAY FLUORESENCE ANALYSES

Figure 3 shows an unheated (control) sample and Figure 4 shows the samples heated at 900, 1000 and 1100°C. In these tests it was visually evident that the glass sheets melted together. As will be shown in Figures 6 and 7, such 'soldering' did not occur at the 760°C experiment. Slices 1 mm thick were cut (vertically) from the center and the sides of the samples and were analyzed by microbeam X-ray fluorescence at beamline X26A at the National Synchrotron Light Source (NSLS) of Brookhaven National Laboratory.

4.1. Method

The intensity of the X-ray beam produced at the NSLS is approximately 10 000 times greater than that produced by conventional laboratory X-ray sources. The X-ray beam also has a very small angular divergence due to the small cross-section of the electron source, and therefore, intense X-ray beams of the order of 5–10 μm diameter can be produced using focusing optics. The X26A beamline at the NSLS was used for these experiments. The beam was tuned to 26·8 keV using a Si (111) monochrometer. This energy allowed excitation of Cd but not Te. Data were collected for Cd, Ca, Zr, and Sr Kα fluorescence. The spot size was focused to 30 × 30 μm using Rh coated Kirckpatrick–Baez mirrors. Energy dispersive SXRF data were collected using a Canberra SL30165

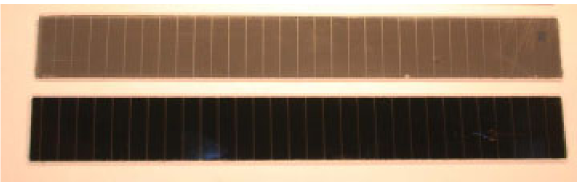

Figure 3. Top and bottom of an unheated sample

Figure 4. (a) Sample after being heated up to 900°C for 1 h; (b) after being heated up to 1000°C for 2 h; (c) after being heated up to 1100°C for 3 h

Si(Li) detector. Incident beam flux was monitored using an ion chamber and changes in fluorescent count rate with time were corrected by normalizing to the ion chamber current values.

Samples were 1-mm-thick slices of the coupons. They were mounted on Kapton tape and placed in a slide holder, with the sample directly exposed to the beam for analysis. Data were collected in two ways. Line scans were collected at step sizes that ranged between 20 and 50 µm, depending on line length. Count times ranged from 5 to 10 s/pixel. Data are shown as normalized Cd counts.

4.2. Results

Figure 5 shows Cd counts along a line scan collected across a slice cut from the control (unheated) sample. The Cd counts in the junction between the two sheets of glass reach a maximum of 50 000 while the Zr counts (indicative of the glass) in the same region are close to zero. Figure 6 shows the Cd line scans collected across the center and edges of a slice cut from the middle of the 760°C PV sample. The Cd count distribution in the center was approximately the same as the distribution in the unheated sample, whereas the distribution near the edges of the PV shows diffusion of Cd in a wider area. Microscopic analysis showed that a gap was created near the edges of the slice; thus, a likely path for Cd loss is from the perimeter of the sample before the two pieces of glass fuse together, as shown in Figure 7.

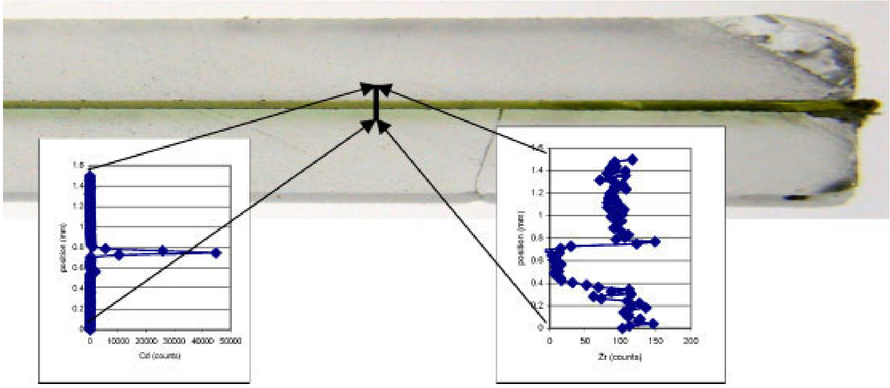

Figure 5. X-ray fluorescence microprobe analysis–vertical slice from unheated (control) sample; Cd and Zr counts

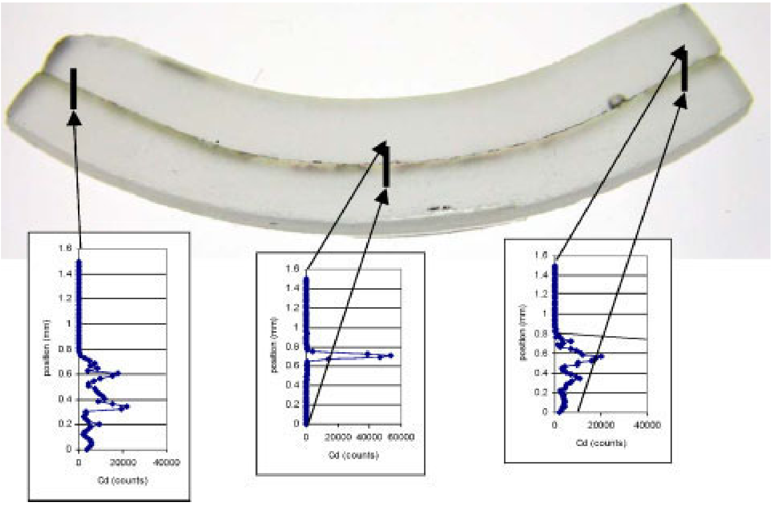

Figure 6. X-ray fluorescence microprobe analysis–vertical slice from middle of sample heated at 760°C; Cd counts in the center and the sides of the slice

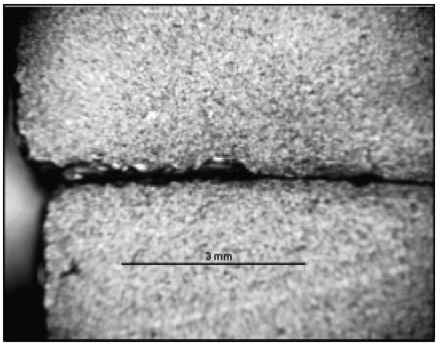

Figure 7. Microphotograph of the edge of a sample heated at 760°C for 30 min

Figure 8 show microprobe results, of a center section from the 1000°C sample and Figure 9 from a side section of the same sample. It is shown that Cd moved to considerable depths into the molten glass and 'froze' there after it cooled. The dispersion of Cd into the glass was more uniform in the side than in the middle of the sample. At the highest temperature we tried (1100°C) Cd diffused into greater depths around the junction

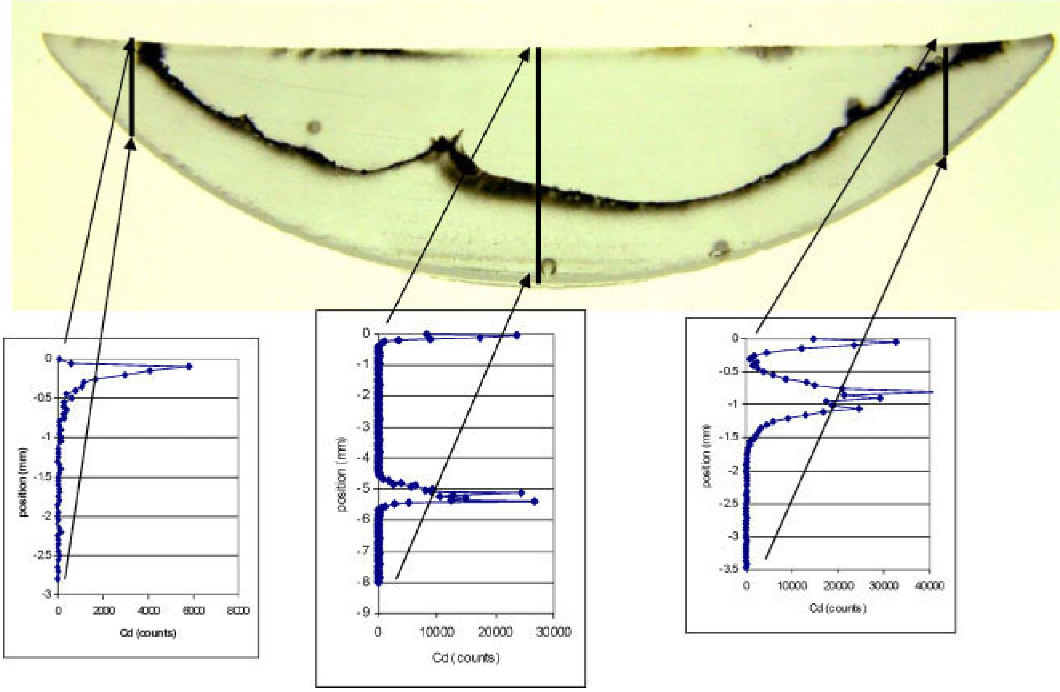

Figure 8. X-ray fluorescence microprobe analysis–vertical slice from middle of sample heated at 1000°C; Cd counts in the center and the sides of the slice

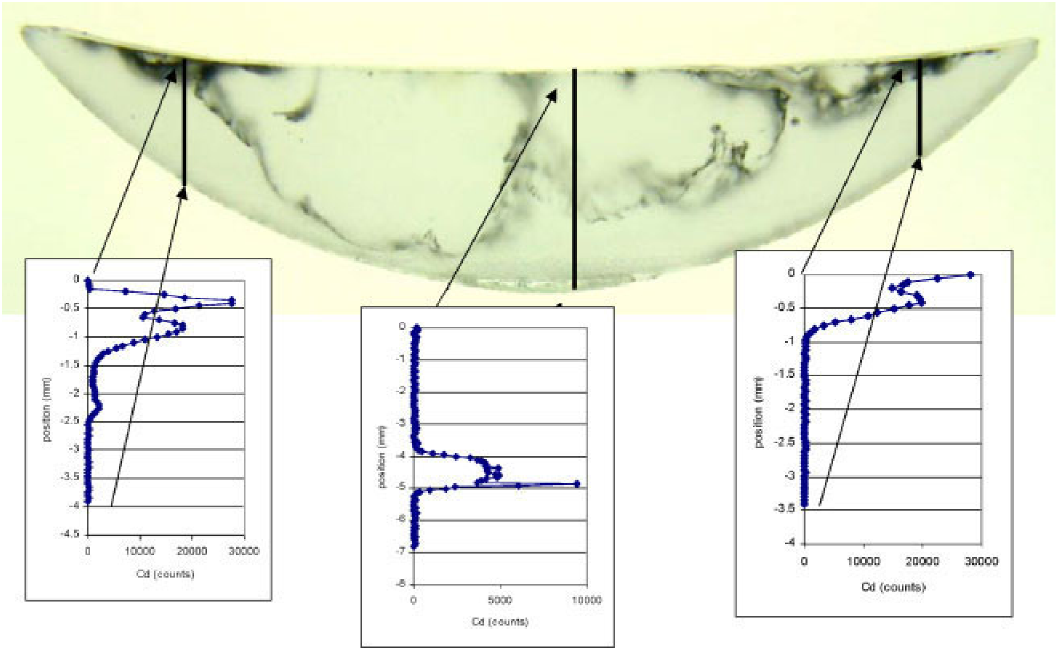

Figure 9. X-ray fluorescence microprobe analysis–vertical slice from side of sample heated at 1000°C; Cd counts in the center and the sides of the slice

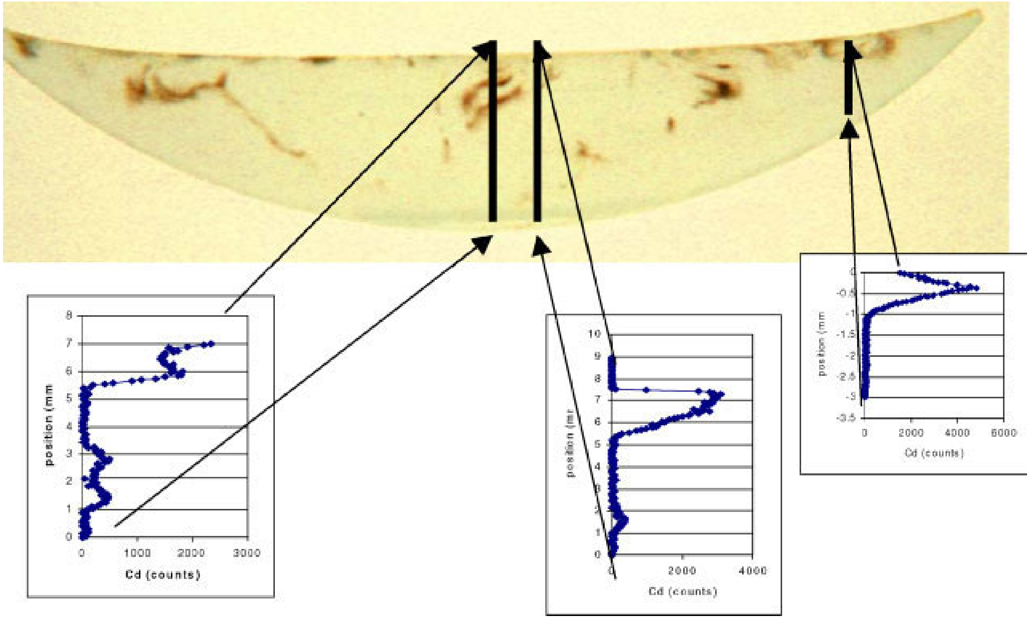

Figure 10. X-ray fluorescence microprobe analysis–vertical slice from middle of sample heated at 1100°C; Cd counts in the center and the sides of the slice

(Figure 10). Although higher temperatures produce greater Cd diffusion, the emissions analyses which show that the Cd loss was the same at all temperatures above 760°C indicate that Cd that has diffused into the glass does not enter the vapor phase in the temperature range of 760–1100°C.

5. ANALYSIS OF THE HEATED GLASS

We followed the standard ASTM C169-89 method[14] for chemical analysis of glass, involving fusion with lithium tetraborate and dissolution in HNO_3. The samples were ground to a fine powder and fused at 1100°C with lithium tetraborate powder (as flux). The fused material was poured into a 20% HNO_3 solution, which was kept at elevated temperature until the fused sample was completely disintegrated and dissolved into the solution. ICP analysis was performed on the solution for cadmium and tellurium. The results of this analysis are shown in Figure 11. The uncertainty of these results is much greater than that the uncertainty of the results presented in Section 3·2 for two reasons: (1) with the exception of the unheated (control) sample, only a small

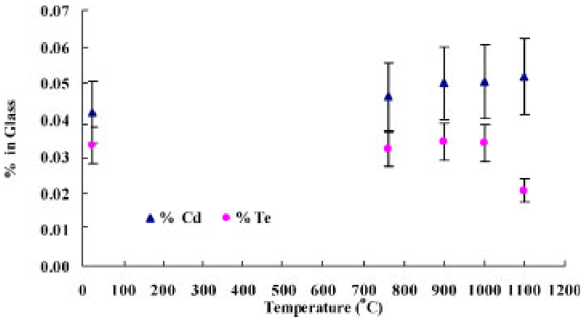

Figure 11. Cadmium and tellurium concentrations in unheated and in molten glass at different temperatures; average values and error bars showing % of error

part of the sample was ground and analyzed, and this may not represent the average concentration in the whole sample; and (2) the salts formed in solution increased the uncertainty of the ICP analysis to about 20% for Cd and 15% for Te.

These experiments showed that the Cd content in the unheated and the heated samples is the same (within the described level of analytical uncertainty), confirming the results of the emissions analysis that Cd was essentially retained in the glass during the heating experiments. The Te concentration in the heated glass, at 1100°C, was lower than the unheated sample, confirming the results of the air emissions analysis showing Te loss at high temperatures.

6. DISCUSSION

Pieces of CdTe PV modules of approximately 25 × 3 cm were heated to temperatures of 760–1100°C following standard UL and ASTM protocols. Four types of analyses were performed: (1) the thermogravimetric analysis showed weight loss of about 2%, which is equal to 77% of the weight of the EVA in the samples; (2) the Cd analyses (using inductively coupled plasma, ICP) showed that the total Cd emissions from each sample was about 3×10^{-4} g which corresponds to about 0·5% loss of the Cd content of the sample. The Te emissions were also very small at the typical residential flame temperatures of 700–900°C, but they were larger at higher temperatures (i.e., 1000–1100°C); (3) the synchrotron-based X-ray fluorescence microprobe analyses clearly show that Cd diffuses into the glass. Comparison of the Cd line scans in the center and the edges of each sample, together with microscopic analysis of the perimeter of the sample, show that the small Cd loss occurs from the edges of the PV module through the space of the two glass sheets before they fuse together. This loss is likely proportional to the ratio of the mass of cadmium (i.e., area of the sample) to its perimeter, and as such would be smaller in full modules. Our samples did not have ‘edge delete’, if the perimeter had a strip free of CdTe, Cd loss could have been even lower. On the other hand, the probability of a module being broken during a fire was not assessed; it is unlikely, however, that a large number of modules could be broken in pieces smaller than our samples; (4) pieces of heated samples were ground and fused with lithium tetraborate powder. The fused liquid was dissolved in HNO_3 and ICP analysis was performed for Cd and Te. The results of this analysis confirm that the Cd content remains constant, thus it is essentially retained into the glass matrix. The Te concentration in the burnt glass, at 1100°C, was lower than the unheated sample, confirming the results of the air emissions analysis showing Te loss at the high temperatures.

A possible explanation for the difference of the behavior of Cd and Te in the highest temperature experiments could be the difference in their oxidation states. Tellurium, when heated to high temperatures, likely oxidizes and subsequently vaporizes. On the other hand, cadmium oxide has a very low vapor pressure even at 1100°C (Figure 1). Additional studies are in progress to investigate the speciation of tellurium and cadmium in the glass matrix.

7. CONCLUSION

Heating experiments to simulate residential fires showed that most (i.e., 99·5%) of the cadmium content of CdTe PV modules was encapsulated in the molten glass matrix. This was confirmed with emissions chemical analysis, synchrotron-based X-ray fluorescence microprobe analysis and chemical analysis of the molten glass. Only $0{\cdot}5 \pm 0{\cdot}1\%$ of the Cd content of each sample was emitted during our tests that cover the wide flame temperature zone of 760–1100°C. The pathway for this loss was likely though the perimeter of the sample before the two sheets of glass fused together. In actual size PV modules, the ratio of perimeter to area is 13·5 times smaller than our sample; thus the actual Cd loss during fires will be extremely small (<0·04% of the Cd content). Multiplying this with the probability of occurrence for residential fires in wood-frame houses in the US (e.g., 10^{-4}), results in emissions of 0·06 mg/GW h (assuming 7 g Cd/m^2, 10% electric conversion efficiency and 1800 kwh/m^2/yr). As discussed in the introduction, the probability of sustained fires in utility systems must be much smaller, due to lack of combustible materials, and, therefore, emissions of cadmium during fires in central PV systems are considered to be essentially zero. The total cadmium emissions during the whole life-cycle of CdTe PV modules (ore mining, metal melting, purification, PV manufacturing) has been estimated to be about 20 mg/GW h.[15] These results apply to glass-to-glass CdTe PV modules which are the only ones in the market. Similarly to Cd, only a tiny percentage of Te was released in the typical residential fire temperature range 760–900°C, but a significant fraction was released at higher temperatures (1000–1100°C).

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Cadmium flows and emissions from CdTe PV: future expectations

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ABSTRACT

Cadmium telluride photovoltaic (CdTe PV) technology is growing rapidly, and already represents the largest contributor to non-silicon based photovoltaics worldwide. We assessed the extent to which CdTe PV will play a notable role in the Cd use and emission flows in the future, and whether it will be environmentally beneficial or detrimental. Our results show that while CdTe PV may account for a large percentage of future global Cd demand, its role in terms of Cd sequestration may be beneficial. We calculated that its potential contribution to yearly global Cd emissions to air and water may well be orders-of-magnitude lower than the respective current Cd emissions rates in Europe.

1. Introduction

Solar electricity is among the most promising forms of renewable energy. Thus, world photovoltaic (PV) production capacity, after having grown by about 40% a year for the best part of the last two decades, accelerated even more in 2006 and 2007. Estimates based on a survey of company statements and press releases from more than 200 companies worldwide indicate that this trend most likely will be maintained into the future, probably surpassing 40 GWp as early as 2012 (Jaeger-Waldau, 2008). Within the whole industry sector, cadmium telluride (CdTe) PV still is a comparatively new and minor player, and so far represents but a negligible fraction of the global demand for primary cadmium (approximately 0.6% in 2008). However, its market share is expanding very rapidly, already representing 5% of the total market for photovoltaics (EPIA and Greenpeace, 2008), with a single producer now supporting a production capacity of 1.1 GW/year (First Solar, 2009a).

Trends in worldwide use and production of cadmium long have caused concern, because of the metal's well-known toxicity; thus, the introduction to the market of a novel cadmium-based technology understandably generated mixed feelings in general public. Accordingly, we undertook a comprehensive prospective analysis to assess whether the often-voiced concern about the possible large-scale negative effects of Cd contamination from CdTe PV might be justified, and to what extent.

We began with a comprehensive review of the most recent information on current cadmium flows in Europe, giving us a reference frame within which to gauge the potential contribution of the possible future large-scale deployment of CdTe PV. The latter was evaluated from the life-cycle inventory (LCI) of current modules, including all related processes, from which we postulated three possible scenarios, based on an update of the results of the EU research project NEEDS (Frankl et al., 2008). We used two common reference time-horizons for drafting our prospective analyses: 2025 and 2050. The assumptions underlying the three scenarios are summarized as follows.

1. 'Pessimistic' scenario: this first scenario assumes that support for the current incentives to the PV sector will not continue long enough for the technology to become competitive with bulk electricity. Consequently, the growth of the whole PV sector is assumed to become stunted. We also considered that the relative market penetration of CdTe PV will remain very low until 2025, with moderate technological improvements that improve efficiency and reduce material demand per unit of output only happening in the last two-and-a-half decades (2025–2050).
2. 'Reference' scenario: PV market growth in this intermediate scenario essentially conforms to the latest predictions by the European PV industry association (EPIA and Greenpeace, 2008) till 2025, and is followed by a gradual reduction in the annual growth rate. CdTe PV is presumed to keep growing at a faster relative pace, reaching 45% of the total PV market by 2025, concurrent with large gains in efficiency and reduced material demand. By 2050, newer, 'third-generation' PV devices are assumed to have overtaken CdTe PV as a widespread alternative, capturing approximately one third of the market, and thus reducing the relative share of CdTe PV to approximately 35%.
3. 'Optimistic' scenario: in this last scenario, bolder annual growth rates are assumed for PV from as early as 2010, and

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the trend is expected to demonstrate quadratic growth through to 2050. The relative role of CdTe PV within the PV sector is assumed to be the same as in the reference scenario, except that in this scenario, we set an upper boundary of 1 TWp for the cumulative installed capacity of CdTe PV by 2050, to account for possible constraints in the supply of tellurium (Fthenakis, 2009).

In all three scenarios, we made the same conservative assumptions about the foreseeable increase in global Cd recycling rates, i.e. from the current 17.5–20% in 2025, and to 30% in 2050. Table 1 lists the specific assumptions on CdTe PV system efficiencies, lifetimes, and installed capacities.

2. Cadmium sources and uses

Cadmium occurs in small amounts in zinc ores, so that Zn producers do not have the option of not mining Cd. Zn extraction and processing have grown for the last three decades, from approximately 5.5 million tonnes per year in the early 1970s to about 11 million tonnes per year today (USGS, 2009a, 2009b). In contrast, total (primary+secondary) Cd demand expanded much more slowly in the 1970s and ’80s, and since remained virtually stable at roughly 20,000 tonnes/year (USGS, 2009a, 2009c). In fact, since the global production of Zn has increased much faster than the corresponding demand for Cd, the annual amounts of raw Cd generated are entirely determined by Zn production rates.

We calculated that the global potential production of primary Cd from processing Zn ores was approximately 33,000 tonnes per year, based on an average Cd/Zn ratio in the ores of 0.003 (UNEP, 2006). This translates into a surplus of nearly 50% of primary Cd over the actual marketed amount; it is not accounted for officially, and remains stockpiled as an unrefined raw metal at zinc mining or refining sites, or is otherwise ‘lost’ to the environment. While these Cd stocks are not reported, nor even classifiable as actual emissions, the sheer lack of information on their management fuels concerns about their adverse environmental effects.

There are four principal industrial uses for cadmium: rechargeable (NiCd) batteries (82%), pigments (10%), plating (6%), and plastic stabilizers (1.5%) (UNEP, 2006; ICdA, 2005). In 2008, the new sector, CdTe PV, absorbed a quantity of Cd corresponding to about 0.6% of reported total Cd use in 2005. We underline here an important differentiation between batteries and PV on one side, and pigments, plating, and stabilizers on the other: while Cd is present in the former applications in self-enclosed compartments and can be fully recycled (at least in principle), the latter three applications are dissipative ones, and thus an inevitable source of eventual Cd contamination.

There is considerable uncertainty on the potential long-term change in global demand for NiCd batteries; however, it seems reasonable to assume that there should not be any major changes ahead in the next two–three decades compared to the last 10–15 years. Hence, for our prospective analysis, we decided to keep constant the current value of the yearly global Cd use for NiCd batteries. For all the other sectors analyzed, there is little reason to doubt that the present exponentially decreasing trend will be maintained, and we made our projections accordingly, employing regression equations.

We then integrated these extrapolated trends with our projections about the future development and deployment of CdTe PV according to the three scenarios discussed in Section 1 (Fig. 1). Depending on the assumptions, up to 15% of global Cd demand will be allocated to CdTe PV in 2050 (Table 1).

3. Cadmium emissions

The information on direct Cd emissions flows is fragmentary, and all inventories carry varying degrees of uncertainty. In our study, we collected the results of the two most relevant, up-to-date European research projects (ESPREME, 2006; ECB, 2007), and integrated them to encompass the full body of 27 countries constituting the European Union (EU-27).

By and large, the major source of yearly Cd emissions to air in Europe is the combustion of fossil fuels in coal- and oil-fired power plants and boilers, accounting for over 60% of the total. The average Cd content in coal reportedly ranges from 0.1 g/tonne (Pacyna and Pacyna, 2001) to 3 g/tonne (Swaine, 1995); petroleum oil has a comparatively lower Cd content, ranging 0.002–0.2 g/tonne (Karlsson et al., 2004). Other important sources of atmospheric Cd emissions are from producing and recycling galvanized iron and steel, as well as the life cycle of non-ferrous metal industrial products containing Zn, together adding up to approximately 15% of the total emissions. A third relevant source is the cement sector, contributing over 10% of the total. All other sectors, including the full life cycle of NiCd batteries (accounting for 82% of the total Cd demand) cumulatively add up to the remaining 15%.

The most pertinent sources of emissions to water again are the metal industries (71% of total), and the phosphate-fertilizer sector (approximately 20% of total), which is also principally responsible for the direct Cd pollution of agricultural soil. The sedimentary phosphate rocks from which virtually all the commercial phosphate is produced naturally contain cadmium

Table 1
Cd demand scenarios for CdTe PV in 2025 and 2050.

Year and scenario	CdTe PV module efficiency(%)	Cd Te PV module lifetime (years)	Cd demand for PV modules (g/kWp)[a]	Cumulative installed capacity (GWp)	Yearly primary Cd demand for CdTe PV (tonnes)	Percentage of yearly global primary Cd demand[b] (%)
2008 ‘Base year’	10.5	30	165	1.2	100	0.6
2025 ‘Pessimistic’	12.5	30	97	25	149	1.0
2025 ‘Reference’	13.5	30	90	195	1790	11
2025 ‘Optimistic’	14.5	30	84	260	2700	16
2050 ‘Pessimistic’	12.5	30	69	240	324	2.2
2050 ‘Reference’	14	30	62	820	1310	8.5
2050 ‘Optimistic’	16	35	54	1000	2440	15

[a] System installed capacity, assuming a performance ratio of 80%. Cd utilization rate is considered to remain at its current level. CdTe and CdS layer thicknesses for 2008, respectively, were assumed for current ‘base year’ modules, and reductions of 30% and 50% of these thicknesses, respectively, were assumed for 2025 and 2050 (the latter is a conservative estimate based on the information on past reductions in Cd use for module manufacturing, i.e. −30% from 2005 to 2008. Data provided by First Solar Inc. (2009)).

[b] Assuming constant primary Cd demand for NiCd batteries and diminishing demand for other sectors (pigments, plating, and plastic stabilizers).

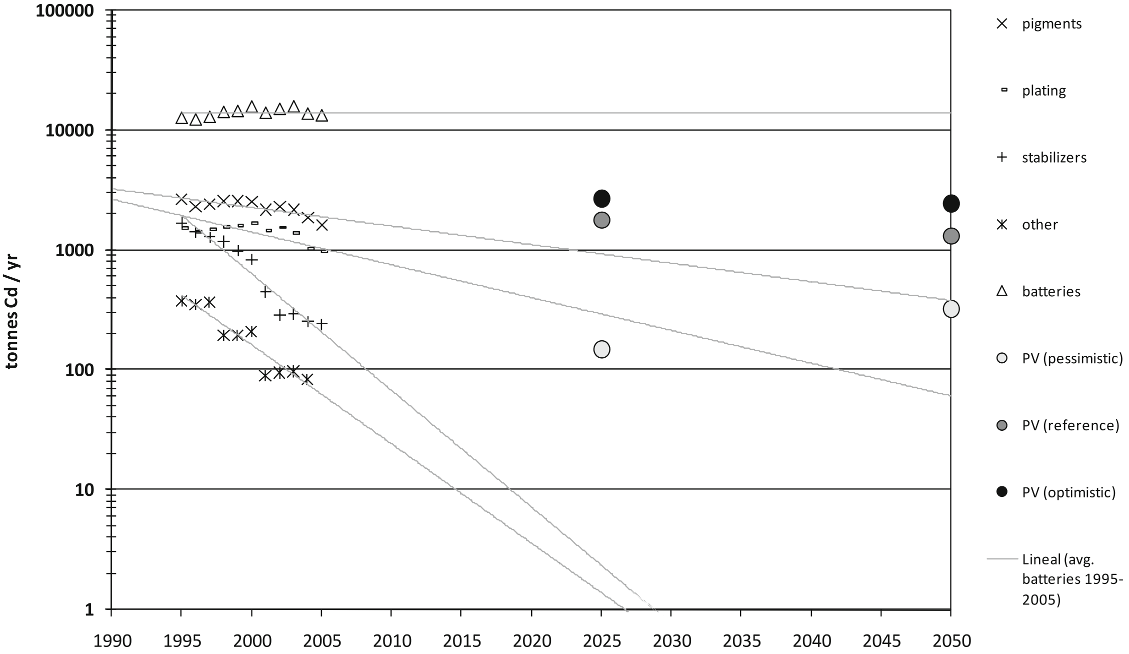

Fig. 1. Historical data and projections for world primary cadmium use by application, from 1990 to 2050 (logarithmic scale).

in concentrations from about 15 to over 200 mg (Cd)/kg (P_2O_5) (EC, 2001; Oosterhuis et al., 2000).

Fig. 2 summarizes this information in a flow-chart form, wherein the thicknesses of the arrows representing Cd-emission flows to water (5), soil (6) and air (7) are proportional to their corresponding magnitudes (tonne/year). The main conclusion from these findings is that the use of resources containing Cd as an impurity (i.e. fossil fuels and phosphorous oxides) and dissipative uses of the metal (e.g. alloys, pigments, and coatings) unquestionably are the greatest sources of life cycle Cd contamination. Public attention and policies first should be directed at curbing these to the maximum extent possible.

Combining the results of a life cycle study based on the current state-of-the-art of CdTe PV with these development scenarios, we then assessed the likely range of global emissions to air due to this technology up to 2050.

To track Cd emission flows, the life cycle of CdTe PV can be subdivided into four stages: (i) Cd extraction and refining, (ii) CdTe-powder production and PV-module manufacturing, (iii) PV-module use, and (iv) PV-module decommissioning. We also included the life cycle of balance of system (BOS) components in our analysis, assuming a typical modern power-plant scale installation (Mason et al., 2006).

(i) Cadmium production is driven entirely by Zn production; therefore, in accordance to the ISO standard 14044 (ISO, 2006), the emissions in the mining and Zn refining are entirely allocated to zinc. The emissions in all the steps following the formation of Cd sponge to the production of 99.999% pure Cd are allocated to the latter.

(ii) Cd emissions to air during Cd purification and CdTe production were estimated by Fthenakis (2004) to be 12 mg(Cd)/kg (Cd production). In the current vapor transport deposition-based manufacturing, the total Cd emissions from all manufacturing and recycling operations are 0.4 mg Cd/kg Cd input[1]. Including all the items in the life cycle inventory of PV-module manufacturing, we calculated here a total of 1.3 mg (Cd)/m^2 of module. It is noteworthy that by far the largest share of these emissions is unrelated to the specific PV technology being employed (e.g. tempered glass, EVA and the transparent conductive oxide (TCO) play a relevant role). BOS components contribute with an additional 0.4 mg (Cd)/m^2 (i.e. 25% of the total), which are mainly due to the steel for the support structure and the fuel used for construction. Water discharges are cleaned to below permissible limits (in Germany below 0.07 ppm) and there are no discharges to soil in the current CdTe PV manufacturing plants. The total Cd in liquid effluents is about 300 g/100 MW production[1], i.e. 0.3 mg (Cd)/m^2. According to the main source used for background data (Ecoinvent, 2007), an additional 0.8 mg (Cd)/m^2 are emitted to freshwater through the production of the TCO and tempered glass. Finally, BOS components add another 2.0 mg (Cd)/m^2 (i.e. 60% of the total), again mainly because of the steel structure.

(iii) Virtually no emissions are associated with the use phase, because cadmium in CdTe PV modules is present only as chemically stable compounds (i.e. CdTe and CdS) that are enclosed and sealed within two glass panes. Thus, we do not expect any emissions, while the modules are in place. Experimental tests showed that even in accidental fires, CdTe would be captured in the molten glass and very little could be released into the environment (Fthenakis et al., 2005).

(iv) For the disposal phase, we assumed that all the CdTe PV modules will be recycled at the end of their useful life (Fthenakis, 2009); BOS components were also assumed to be recycled for the most part, except for the concrete foundations, which were assumed to be left on site. No environmental credits were assigned for the materials sent to recycling (open-loop model). The current leading manufacturer (First Solar) implemented a take-back policy, setting aside sufficient funds to meet the estimated costs of collecting and recycling modules (First Solar, 2009b). Future competing manufacturers are likely to follow this example, and, indeed, this already has happened in at least two instances (PrimeStar Solar, 2009; Abound Solar, 2009). The recycling method, we analyzed in this study, is the only one that was tested on a full-production scale by the world's leading producer of CdTe modules (Sander et al., 2007);

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[1] Data provided by First Solar Inc. (2009)

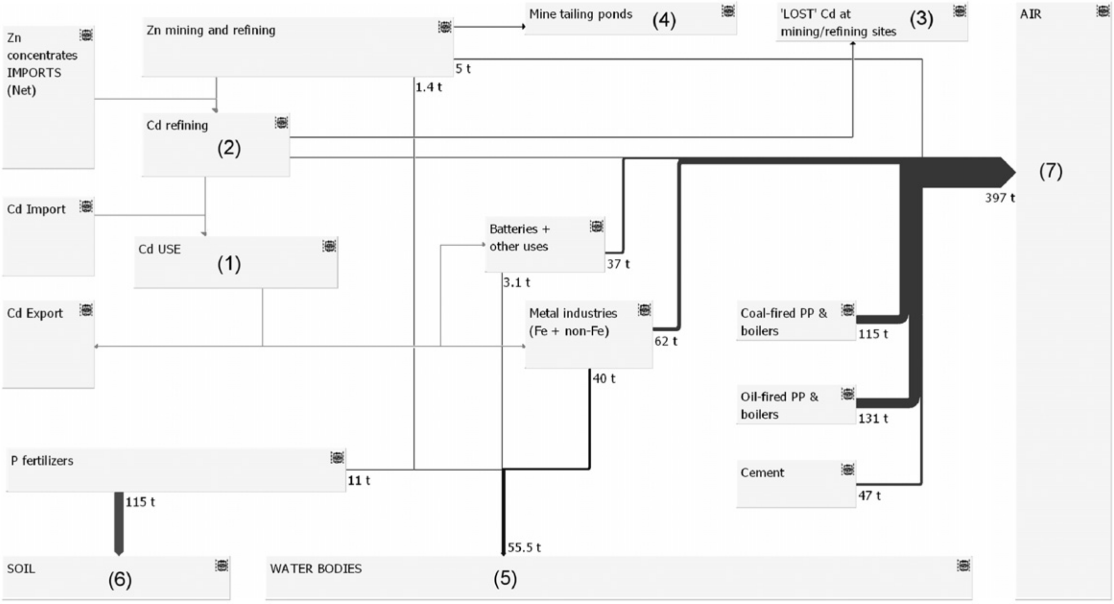

Fig. 2. Flowchart of current Cd flows in EU-27. Arrow thicknesses for all Cd-emission flows to water (5), soil (6), and air (7) are proportional to the corresponding magnitudes (tonne/year).

Table 2
Cd emission scenarios for CdTe PV in 2025 and 2050.

Year and scenario	Global Cd emissions to air due to CdTe PV (kg/year)	As relative to current Cd emissions to air in EU-27 (%)	Global Cd emissions to water due to CdTe PV (kg/year)	As relative to current Cd emissions to water in EU-27 (%)
2008 ‘Base year’	0.8	0.0002	2.0	0.004
2025 ‘Pessimistic’	17	0.0043	40	0.07
2025 ‘Reference’	130	0.033	310	0.56
2025 ‘Optimistic’	170	0.043	400	0.72
2050 ‘Pessimistic’	100	0.025	240	0.42
2050 ‘Reference’	320	0.080	760	1.4
2050 ‘Optimistic’	350	0.088	840	1.5

detailed inventory data were made available. The spent PV modules are cut and then crushed into pea-sized fragments, and leached in a dilute solution of sulphuric acid and hydrogen peroxide. Cd, Te, and Cu are precipitated from the solution together; the recovered filter cake finally is sent out for re-processing into high-purity metals. We omitted the re-processing of the filter cake from our analysis, adopting instead an open-loop recycling model according to which the Cd is attributed entirely to those other product systems that then use the purified metals (Guinée, 2001). The recycling processes employs 99.97% efficient HEPA filters throughout, so that Cd emissions to air from crushing operations are effectively captured. As mentioned above, the total residual emissions from all production and recycling operations are 0.4 mg Cd/kg Cd. We calculated Cd emissions to water by taking for granted that the treatment of the waste-water effluents assures they meet the current European limit of 0.2 ppm for cadmium (Council Directive 83/513/EEC); the resulting discharge rate is approximately 1 mg of Cd per square metre of decommissioned PV module. Actually, the currently operating facility in Frankfurt–Oder complies with an even lower threshold level (i.e. 0.07 ppm of Cd).

We then calculated the average yearly Cd emissions associated with CdTe PV in our three future scenarios by supposing that the modules' characteristics remain at their initial values up to the end of the time spans considered (i.e. 2008–2025 and 2026–2050), and discounting them per-kWp over the respective module lifetimes. All emissions are calculated on the basis of the full life cycle of the PV system, i.e. they include manufacturing and end of life of both the PV modules and BOS. Table 2 gives our results.

We note that these values can be regarded as the ‘worst case’ predictions for Cd emissions, since reasonably we can assume that changes in module characteristics will be gradual rather than abrupt, resulting in correspondingly better performance earlier (for instance, Cd use for module manufacturing in 2008 is already down by approximately 30% compared to 2005 levels). Also, a sizeable fraction of these Cd emissions are due to non-technology specific inputs (e.g. TCO and glass) and the steel-based support structure; both these contributions could be heavily reduced in the future, for instance switching to alternative encapsulation substrates and/or support materials (e.g. wood).

Fig. 3 presents a general overview of the current cadmium flows in the EU-27 (wherein items are numbered in the same way as in Fig. 2), and compares them to the findings from our prospective analysis of the potential global Cd emissions to air and water due to a large-scale deployment of CdTe PV in 2025 and 2050. Error bars are provided, indicating, respectively, +/−50% for EU flows, and the range of our three scenarios for the future global emissions due to CdTe PV.

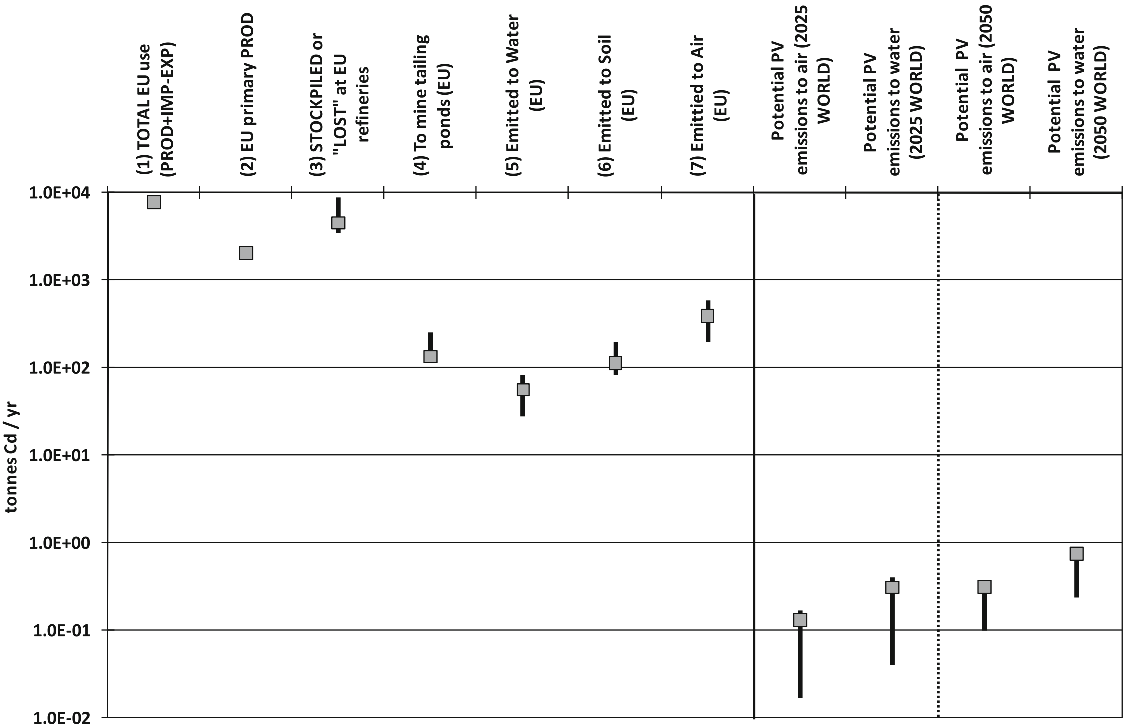

Fig. 3. Current Cd flows in EU-27 compared to potential future global Cd emissions caused by CdTe PV (logarithmic scale). Assumed maximum cumulative capacities are 260 GWp in 2025 and 1 TWp in 2050. Numbers in parenthesis (1–7) refer to corresponding flows in Fig. 2.

4. Discussion and conclusions

As is common in long-term prospective studies, an inevitable range of uncertainty remains, reflecting, on the one hand, the intrinsic variability in the life-cycle inventory databases, and on the other hand, the different assumptions made in the three scenarios. However, we are strikingly reassured after comparing the findings from our prospective *global* analysis to the current routine Cd flows in the EU-27.

Firstly, since cadmium is contained in zinc ores, is inevitably mined with them and generated as a by-product or a waste product of the Zn production, the increased usage of CdTe photovoltaics may be regarded as beneficial to the global environment by effectively sequestering a non-negligible amount of cadmium from otherwise potentially harmful left-over stockpiles.

Secondly, even under the largest growth scenario of 1 TWp of installed CdTe PV power in 2050, the related Cd emissions to water and air, would be lower by at least two and three orders-of-magnitude than the present yearly Cd emissions within the EU-27 alone. It is also noteworthy that whenever CdTe PV specifically replaces coal in power generation, it lowers by 100–360 times the associated Cd emissions to air (Fthenakis, 2004).

In conclusion, our prospective life cycle analysis suggests that a large growth in the CdTe PV sector has the potential to actually reduce, rather than increase, overall global cadmium-related environmental pollution.

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FATE AND TRANSPORT EVALUATION OF POTENTIAL LEACHING RISKS FROM CADMIUM TELLURIDE PHOTOVOLTAICS

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Abstract—Fate and transport analysis has been performed to evaluate potential exposures to cadmium (Cd) from cadmium telluride (CdTe) photovoltaics (PV) for rainwater leaching from broken modules in a commercial building scenario. Leaching from broken modules is modeled using the worst-case scenario of total release of Cd, and residential screening levels are used to evaluate potential health impacts to on-site workers and off-site residents. A rooftop installation was considered rather than a ground-mount installation because rainwater runoff is concentrated via building downspouts in a rooftop installation rather than being dispersed across large areas in a ground-mount installation. Fate and transport of Cd from leachate to soil are modeled using equilibrium soil/soil-water partitioning. Subsequent migration to ambient air as windblown dust is evaluated with a screening Gaussian plume dispersion model, and migration to groundwater is evaluated with a dilution-attenuation factor approach. Exposure point concentrations in soil, air, and groundwater are one to six orders of magnitude below conservative (residential soil, residential air, drinking water) human health screening levels in both a California and southern Germany (Baden-Württemberg) exposure scenario. Potential exposures to Cd from rainwater leaching of broken modules in a commercial building scenario are highly unlikely to pose a potential health risk to on-site workers or off-site residents. Environ. Toxicol. Chem. 2012;31:1670–1675. © 2012 SETAC

Keywords—Cadmium telluride Leaching Risk assessment Fate and transport Cadmium telluride photovoltaics

INTRODUCTION

Solar energy is an important technology for climate change mitigation and development of a low carbon economy because it offers the highest global technical potential for electricity generation among renewable energy sources [1]. In particular, cadmium telluride (CdTe) thin film photovoltaic (PV) modules have the lowest life cycle carbon footprint and fastest energy payback time of current PV technologies [2]. Although CdTe has been shown to be significantly less toxic than elemental cadmium (Cd) on an acute basis [3], the primary health and safety concern for CdTe PV is the potential introduction of Cd compounds into the environment. When considered on a life cycle basis from raw material acquisition through product end-of-life, CdTe PV has been found to produce environmental Cd emissions to air that are no higher than those from conventional silicon PV technologies [4,5]. Moreover, because Cd is an unavoidable by-product of Zn mining, large-scale deployment of CdTe PV sequesters waste Cd that would otherwise be disposed of [6]. Prefunded end-of-life takeback and recycling programs also significantly reduce the overall environmental impact of CdTe PV modules [7].

Under normal operation, CdTe PV modules do not pose a threat to human health or the environment, because during the manufacturing process, the CdTe semiconductor layer is bound under high temperature to one sheet of glass, coated with an industrial laminate material, and then encapsulated between a second sheet of glass. However, some stakeholders have raised concerns about the potential exposure to CdTe from leaching of broken modules, defined as modules with cracked glass or broken pieces. Breakage results from extreme weather or human factors. Although rare, breakage followed by precipitation may potentially result in leaching of CdTe from modules and subsequent exposure to Cd compounds in soil, air, or groundwater. This analysis uses fate and transport modeling to estimate potential exposures to Cd compounds resulting from leaching and then evaluates the potential health effects associated with these exposures.

Fate and transport scenarios were evaluated for two geographic locations, southern Germany and California. Germany is among the world's leading PV markets, having accounted for nearly half of global demand in 2010 [8]. This analysis focuses on the higher solar irradiance region of southern Germany (Federal State of Baden-Württemberg). California is a leading PV market in the United States, and in 2011, the California state legislature adopted a renewable portfolio standard of 33% by 2020 (http://www.cpuc.ca.gov/PUC/energy/Renewables/index.htm).

In the present analysis, a commercial building scenario was chosen rather than a residential building scenario because the larger PV array size for commercial buildings increases the probability that module breakage may occur in a given year. However, both nonresidential (on-site) and residential (off-site) exposure scenarios were considered and evaluated using residential screening values. A rooftop installation was considered rather than a ground-mount installation because rainwater runoff can be concentrated via building downspouts in a rooftop installation (impact via concentrated stream) rather than being dispersed across large areas in a ground-mount installation. The evaluation considers the worst-case scenario in which the total mass of Cd in each broken module is released.

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MATERIALS AND METHODS

The present analysis considers broken CdTe PV modules located on the rooftop of a commercial building. Potential receptors considered for analysis include on-site commercial/industrial workers and off-site residents. Under this exposure scenario, potential exposure to Cd is considered for commercial/industrial workers via inhalation of, dermal contact with, and ingestion of Cd leached into soil, as well as exposure to groundwater potentially impacted by leachate. Also under this exposure scenario, potential exposure to Cd is considered for off-site residents via inhalation of windblown dust from affected soil and exposure to groundwater potentially impacted by leachate.

To characterize these potential exposure scenarios, exposure point concentrations of Cd in soil, air, and groundwater are estimated using a fate and transport analysis. The estimated exposure point concentrations are the relevant concentrations to which on-site workers or off-site residents may potentially be exposed. The exposure point concentration for soil is only relevant to the on-site worker who may potentially have incidental contact with on-site surface soil during the workday. The exposure point concentration for air is relevant to both the on-site worker and off-site resident who may potentially inhale affected ambient air. The exposure point concentration for groundwater is relevant to both the on-site worker and off-site resident who may potentially use groundwater as drinking water.

To evaluate potential human health impacts, estimated exposure point concentrations are compared to human health screening levels. Nonresidential screening levels are applicable to the on-site worker, whereas residential screening levels are applicable to the off-site resident. In this evaluation, the residential screening levels are used in comparison with estimated exposure point concentrations to be protective of both on-site workers and off-site residents. Specifically, for California, residential screening levels for soil (1.7 mg/kg) and air (1.4×10^{-3} μg/m^3) are used instead of commercial/industrial screening levels of 7.5 mg/kg and 6.8×10^{-3} μg/m^3, respectively. For Germany, a residential screening level for soil (2 mg/kg) is used instead of a commercial/industrial screening level of 60 mg/kg.

The fate and transport methodology used to estimate migration of Cd from the emission point (broken module) to the exposure point (soil, air, or groundwater) is summarized in Figure 1 and described with Equations 1 to 5 below. The concentration of Cd in leachate resulting from rainwater that falls upon and runs off broken modules is estimated based on a worst-case mass balance approach, where all the mass of Cd in each broken module is assumed to be transferred from the module into the volume of rainfall that falls upon the module during the exposure period. The subsequent concentration of Cd in rainwater runoff from the overall module array is calculated using a weighted average between impacted runoff from broken modules and nonimpacted runoff from unbroken modules. It should be noted that the assumption of total release of Cd from a broken module was adopted for the purpose of conducting screening level risk assessment, but is unlikely in the light of low experimentally measured emissions from broken or burnt modules [4].

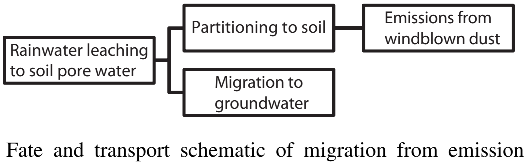

Fig. 1. Fate and transport schematic of migration from emission point (rainwater leaching from broken module) to exposure point in soil, air, and groundwater.

It is assumed that the rooftop runoff is conveyed via downspouts and discharged onto the ground surface over an area of 1 m^2 per downspout. Chemical concentrations in vadose (unsaturated) zone soil pore water at these discharge locations are assumed to be equal to the concentrations in the rooftop runoff discharge. The vadose zone soil pore water throughout the rest of the site is assumed to be nonimpacted. For the commercial building scenario, a roof with dimensions of 50×50 m is assumed to be completely covered by CdTe PV modules of dimensions 0.6×1.2 m each. Twenty-five downspouts are assumed for the building, based on the roof area being 25 times larger than a standard residential building (10×10 m) [9], where the latter would have one downspout.

The vadose zone soil pore water concentration in each 1 m^2 downspout ground surface area is estimated with the worst-case mass balance approach in Equation 1, where the numerator represents the total annual release of Cd and the denominator represents the total annual column of rainfall.

$$\mathrm{CV} = \frac{N \times M \times \mathrm{CF} \times B}{P \times A} \tag{1}$$

where CV is the Cd concentration in vadose soil pore water (mg/L); N is the number of modules (unitless); M is the mass of Cd per module (g); CF is the conversion factor (mg/g); B is the module breakage rate (year^{-1}); P is the annual average precipitation (L/m^2-year), which is annual precipitation (m/year) falling over 1 m^2 converted to units of L from m^3; and A is the area of roof-top array (m^2).

The potential transport of Cd to soil is evaluated in accordance with the equilibrium-partitioning approach described in the U.S. Environmental Protection Agency (U.S. EPA) soil screening guidance [10,11]. It is assumed that the surface soil where rainwater runoff is discharged is instantaneously impacted with Cd, at the concentration predicted by equilibrium partitioning between the water and soil matrices, as expressed by the soil/soil-water partitioning coefficient (K_d) value for Cd (Eqn. 2).

$$\mathrm{CS_{eq}} = \mathrm{CV} \times \left(K_\mathrm{d} + \frac{\theta_\mathrm{w}}{\rho_\mathrm{b}}\right) \tag{2}$$

where $\mathrm{CS_{eq}}$ is the equilibrium concentration of Cd in impacted soil (mg/kg); CV is the concentration of Cd in vadose zone soil pore water (mg/L); K_d is the soil/soil-water partitioning coefficient (L/kg); θ_w is the soil water-filled porosity (unitless); and ρ_b is the soil dry bulk density (kg/L).

For this scenario, it is assumed that the entire area of the site evaluated here is uncovered by concrete or asphalt and is open bare soil to allow the runoff water to penetrate into site soils. In actuality, commercial sites are often completely covered by concrete or asphalt. On-site commercial/industrial workers are assumed on average to be exposed to site soils across the entire portion of the site that is not occupied by the building. Exposure point concentrations of chemicals in soil are therefore calculated as site-wide average concentrations, incorporating areas of impacted soils (at the worst-case concentrations predicted by equilibrium partitioning) and nonimpacted soils (Eqn. 3). The exposure area (SA-A; Fig. 2) is assumed to be the same as that for a residential building [9], even though a commercial building property would likely be larger, therefore with larger

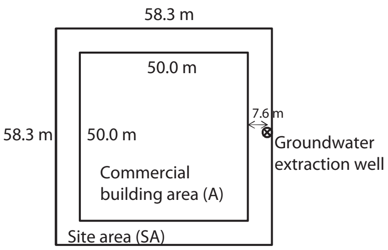

Fig. 2. Site schematic.

nonimpacted areas. This assumption accounts for the potential of at least part of the site to be covered.

$$\mathrm{CS} = \mathrm{CS_{eq}} \times \frac{\mathrm{IA}}{(\mathrm{SA} - A)} \tag{3}$$

where CS is the exposure point concentration of Cd in soil (mg/kg); $\mathrm{CS_{eq}}$ is the equilibrium concentration of Cd in impacted soil (mg/kg); IA is the impacted area (m^2); SA is the site area (m^2); and A is the area of building (m^2).

The potential transport of Cd from impacted soil to ambient air is estimated (Eqn. 4) using the U.S. EPA-recommended default windblown dust emissions flux for wind erosion (1.38×10^{-7} g/s-m^2) [11]. As noted above, the uncovered portion of the site is assumed to be bare earth for the purpose of this analysis, whereas commercial sites are frequently landscaped or covered by concrete or asphalt. It is assumed that Cd is present in this windblown dust at the soil concentration predicted by equilibrium partitioning (Eqn. 2). The U.S. EPA screening Gaussian plume dispersion model SCREEN3 [12] is used in conjunction with the emissions flux to estimate worst-case concentrations of dust and thus Cd in ambient air. The maximum hourly dust concentration from SCREEN3 was adjusted with a persistence factor of 0.08 [13] to derive the annual worst-case concentrations of dust.

$$\mathrm{CA} = \mathrm{CS_{eq}} \times \mathrm{CD} \times \mathrm{CF_1} \times \mathrm{CF_2} \tag{4}$$

where CA is the exposure point concentration of Cd in air (μg/m^3); $\mathrm{CS_{eq}}$is the equilibrium Cd concentration in soil (mg/kg); CD is the worst case dust concentration in air (mg/m^3); $\mathrm{CF_1}$ is the conversion factor (kg/mg); and $\mathrm{CF_2}$ is the conversion factor (μg/mg).

The potential transport of Cd to groundwater is evaluated in accordance with the dilution-attenuation factor (DAF) approach described in the U.S. EPA soil screening guidance [10,11]. It is assumed that vadose zone soil water, from the ground surface to the groundwater table, contains Cd at the module array-runoff concentration discussed above in Equation 1 (i.e., it is assumed the soil column does not adsorb any Cd). The potential concentration of Cd in groundwater at the hypothetical point of usage, which is assumed by the model to be a groundwater extraction well located 25 ft from the edge of the impacted area, is calculated by applying an upper bound (95th percentile) DAF [14] to the vadose soil water concentration (Eqn. 5). Note that for DAF values, higher percentiles represent numerically lower values, indicating less dilution-attenuation, and therefore higher groundwater concentrations.

$$\mathrm{CW} = \frac{\mathrm{CV}}{\mathrm{DAF}} \times \mathrm{CF} \tag{5}$$

where CW is the exposure point concentration of Cd in groundwater (μg/L); CV is the concentration of Cd in vadose zone soil pore water (mg/L); DAF is the dilution-attenuation factor (unitless); and CF is the conversion factor (μg/mg).

The specific fate and transport modeling parameters used in Equations 1 to 5 are summarized in Table 1. The parameters are the same for the two geographies evaluated, with the exception of higher average annual precipitation (37.32 inches/year; http://www2.lubw.baden-wuerttemberg.de/public/abt5/klimaatlas_bw/klima/aenderungen/ba-wue/niederschlag/index.html) for Baden-Württemberg, relative to California (21.44 inches/year; http://www.nationalatlas.gov/printable/precipitation.html). In addition, the German dry soil bulk density (1.4 kg/L; average between settlement and grassland areas [15]) is slightly lower than that used for California (1.5 kg/L [11]).

It should also be noted that the German Federal Environment Ministry does not provide a default value for the soil/soil-water partitioning coefficient data (K_d) for cadmium, due to low mobility in groundwater [16]. In this evaluation, the K_d value used for the California exposure scenario is applied to the southern Germany exposure scenario.

RESULTS

Exposure point concentrations of Cd in soil, air, and groundwater derived in Equations 3 to 5, respectively, are summarized in Table 2, and compared to human health screening levels for each of these media. For the California case, the screening levels in soil, air, and groundwater are from the California Human Health Screening Levels, U.S. EPA Region 9 Regional Screening Levels, and U.S. National Primary Drinking Water Regulations, respectively. Residential soil and indoor air screening values are used, both of which are more protective than the commercial building soil and outdoor air exposure scenarios considered here.

In the southern Germany case, the soil screening level is from the residential trigger value in Annex 2 of the Federal Soil Protection and Contaminated Sites Ordinance (http://www.umweltbundesamt.de/boden-und-altlasten/altlast/web1/berichte/pdf/bbodschv-engl.pdf). The standard residential trigger value in soil is 20 mg/kg, whereas for the special case of gardens in which children stay and food plants are grown, a residential trigger value of 2 mg/kg applies. Table 2 presents the latter more protective soil screening value, which is similar to the California Human Health Screening Levels value used for California. The German air screening level is based on World Health Organization air quality guidelines for Europe [17] and is slightly higher in magnitude than the California air screening level. The groundwater screening level is from the German regulation on drinking water (http://www.umweltbundesamt.de/wasser-e/themen/trinkwasser/gesetze.htm) and is the same as the U.S. drinking water standard.

In the California and southern Germany cases, exposure point concentrations in soil, air, and groundwater are one to six orders of magnitude below human health screening levels, indicating that it is highly unlikely that exposures to these media would pose potential health risks to on-site workers or off-site residents. In particular, air concentrations are below screening levels by five to six orders of magnitude, indicating exposure to ambient air is a de minimis exposure pathway.

For reference, the average background Cd concentration in California surface soils is 0.36 mg/kg [18], whereas average background surface soil Cd concentrations in Baden-Württemberg range from 0.2 to 0.3 mg/kg [19]. Therefore, modeled impacts to soil are over an order of magnitude below both human health screening levels and regional background levels.

Table 1. Fate and transport modeling parameters used in conjunction with Equations 1 to 5 for California (CA) and Baden-Württemberg (B-W) exposure scenarios[a]

Equation 1 parameters[b]	Equation 2 parameters[c]	Equation 3 parameters[d]	Equation 4 parameters[e]	Equation 5 parameters[f]
N: 3472	CV (CA/B-W): 0.00612/0.00352 mg/L	CS_{eq} (CA/B-W): 0.460/0.265 mg/kg	CS_{eq} (CA/B-W): 0.460/0.265 mg/kg	CV (CA/B-W): 0.00612/0.00352 mg/L
M: 6 g/module	K_d: 75 L/kg	IA: 25 m^2	CD: 5.5×10^{-6}	DAF: 7.82
CF: 1000 mg/g	θ_w: 0.3	SA: 3400 m^2	CF_1: 0.000001 kg/mg	CF: 1000 µg/mg
B: 0.04% $year^{-1}$	ρ_b (CA/B-W): 1.5/1.4 kg/L	A: 2500 m^2	CF_2: 1000 µg/mg	
P (CA/B-W)[g]: 545/947 L/m^2-year				
A: 2500 m^2				

[a] When two values are provided for a given parameter, first value is for CA and second value is for B-W.

[b] Parameters in Equation 1 are N (number of modules), M (mass of Cd per module), CF (conversion factor), B (module breakage rate), P (annual average precipitation), and A (area of building).

[c] Parameters in Equation 2 are CV (concentration of Cd in vadose zone soil pore water), K_d (soil/soil-water partitioning coefficient), θ_w (soil water-filled porosity), and ρ_b (soil dry bulk density).

[d] Parameters in Equation 3 are CS_{eq} (equilibrium concentration of Cd in impacted soil), IA (impacted area), SA (site area), and A (area of building).

[e] Parameters in Equation 4 are CS_{eq} (equilibrium Cd concentration in soil), CD (worst case dust concentration in air), CF_1 (conversion factor), and CF_2 (conversion factor).

[f] Parameters in Equation 5 are CV (concentration of Cd in vadose zone soil pore water), DAF (dilution-attenuation factor), and CF (conversion factor).

[g] Precipitation parameter (P) is based on annual average precipitation of 21.44 and 37.32 inches for California and Baden-Württemberg respectively.

For further perspective on soil impacts, Cd is commonly found in agricultural fertilizers. California is among the top users of agricultural fertilizer in the United States and analysis of metals in fertilizer samples has been performed by the California Department of Food and Agriculture, with median Cd concentrations of 89 mg/kg in phosphate fertilizer and 37 mg/kg in nitrogen/phosphorus/potassium (NPK) fertilizer [20]. Similarly, average Cd concentrations in phosphate and NPK fertilizer in Germany are 60 and 18 mg/kg, respectively (http://www.bfr.bund.de/cm/343/cadmiumaustrag_ueber_duengemittel.pdf). These values are over three orders of magnitude higher than the estimated exposure point concentration in soil in California and southern Germany (Table 2).

For reference, average background Cd (total suspended particulate) concentrations in California ambient air monitoring stations ranged from 0.0008 to 0.001 µg/m^3 in 2008 (http://www.epa.gov/air/data/geosel.html). Similarly, average background Cd concentrations in Europe range from 0.0001 to 0.0004 µg/m^3 in rural areas and 0.0002 to 0.0025 µg/m^3 in urban areas [21]. Therefore, modeled impacts to air are five orders of magnitude below both health screening levels and background levels.

For reference, the average background Cd concentration in groundwater from 1984 to 2004 in California Air Force bases ranged from <0.004 mg/L (50th percentile) to 0.006 mg/L (95th percentile; http://www.dtsc.ca.gov/assessingrisk/upload/metals_handout.pdf). In Baden-Württemberg, average background Cd concentrations in groundwater range from 0.00052 to 0.0039 mg/L [22]. Therefore, modeled impacts to groundwater in California and southern Germany are below both human health screening levels and background levels.

In addition to soil, air, and groundwater, another route of potential concern is direct discharge of rooftop runoff to stormwater catch basins. In combined sewer systems, stormwater and wastewater are collected together and treated at a publicly owned treatment works (POTW). The worst-case rooftop runoff Cd concentration (assuming total release of Cd from broken modules) is equivalent to the estimated Cd concentration in vadose soil pore water (CV; 0.004–0.006 mg/L; Table 1). Because this concentration is approximately consistent with drinking water standards, impacts to POTW's from rooftop runoff are expected to be minimal.

DISCUSSION

The fate and transport analysis conducted here represents a worst-case scenario of total Cd release from broken modules. An implicit assumption for this scenario is that a broken module would remain undetected and in the field over the exposure duration. This is a screening level assumption that would likely not occur given routine inspections of modules or power output monitoring. For example, the latter may include diagnostic comparison of actual to expected performance or comparison of co-located arrays to identify low performance areas and modules that are nonfunctioning potentially due to breakage.

Another implicit assumption is that emissions of CdTe from rainwater leaching of broken modules can be modeled as emissions of Cd, a "read-across" approach. This is a screening

Table 2. Estimated exposure point concentration (EPC) and corresponding human health screening level in soil, air, and groundwater.

	Soil EPC (mg/kg)	Soil screening level (mg/kg)	Air EPC (µg/m^3)	Air screening level (µg/m^3)	Ground-water EPC (mg/L)	Ground-water screening level (mg/L)
California[a]	1.28×10^{-2}	1.7	2.53×10^{-9}	1.4×10^{-3}	7.83×10^{-4}	5×10^{-3}
Baden-Württemberg[b]	7.35×10^{-3}	2	1.46×10^{-9}	5×10^{-3}	4.50×10^{-4}	5×10^{-3}

[a] California screening levels are from the California Human Health Screening Levels (http://www.calepa.ca.gov/brownfields/documents/2005/CHHSLsGuide.pdf) for soil, USEPA Region 9 (http://www.epa.gov/region9/superfund/prg/) for air, and U.S. National Primary Drinking Water Regulations (http://water.epa.gov/drink/contaminants/index.cfm) for groundwater.

[b] German screening levels are from Annex 2 of the Federal Soil Protection and Contaminated Sites Ordinance (http://www.umweltbundesamt.de/boden-und-altlasten/altlast/web1/berichte/pdf/bbodschv-engl.pdf) for soil, World Health Organization air quality guidelines for Europe [17] for air, and German regulation on drinking water (http://www.umweltbundesamt.de/wasser-e/themen/trinkwasser/gesetze.htm) for groundwater.

level assumption because CdTe is relatively insoluble [3,23]. For example, transformation and dissolution testing is designed to determine the rate and extent to which sparingly soluble metal compounds can produce soluble available ionic species in aqueous media under a set of standard laboratory conditions representative of those generally occurring in the environment. Based on long-term transformation and dissolution testing of CdTe, a 1 mg/L loading showed a concentration of 15 μg of Cd per L after 28 d, indicating approximately 1.5% solubility [24]. This is also consistent with the very low solubility product ($K_{sp} = 9.5 \times 10^{-35}$) for CdTe [25]. In addition to low solubility, CdTe can be contrasted with elemental Cd and other Cd compounds based on limited bioavailability and low acute toxicity, which result in an overall margin of safety of two orders of magnitude likely inherent to CdTe screening assessments developed using the read-across approach from Cd [25].

Because of the low solubility of CdTe, aggressive extraction methods are required to leach CdTe from a module. Such methods are used, for example, in the recycling process for CdTe modules. They involve crushing the module into mm-scale pieces and agitating it in an acidic solution [7]. These extraction methods in no way mimic actual broken or cracked module exposure to rainwater. Therefore, the assumption of total Cd release from broken modules is highly unlikely.

In addition to this worst-case assumption, other upper bound assumptions are used in the analysis. Migration from vadose zone soil pore water to soil is modeled with equilibrium partitioning, which represents the theoretical maximum concentration possible in the solid phase, for a given concentration in soil pore water. Subsequent migration from soil to air is modeled using the SCREEN3 U.S. EPA Gaussian plume dispersion model to estimate worst-case concentrations of windblown dust.

The approach used to estimate groundwater impacts is also upperbound because it does not account for the loss of chemical mass from the pore water during soil-water partitioning, instead assuming that the pore water is instantaneously in equilibrium with the solid soil phase. Accordingly, no mass in pore water is lost to the solid soil phase during partitioning, when in actuality some of this mass partitions into the solid soil phase, with a subsequent reduction in the concentration of Cd in the pore water with depth, until equilibrium is reached. Accounting for the loss of chemical mass from the pore water to the solid phase would lower chemical concentrations in soil water that are assumed to penetrate to groundwater and so reduce predicted groundwater exposures. In addition, the DAF assumes that there is an infinite source of mass available for release. Conserving mass would likely reduce the average long-term groundwater concentration estimated using the DAF approach and so result in lower groundwater exposures. Moreover, the dilution-attenuation factor used was a 95th percentile DAF where the higher percentiles represent numerically lower DAF values, indicating less dilution-attenuation and therefore higher groundwater concentrations. All of these factors contribute to the likelihood that impacts to groundwater are overestimated. Also as described earlier, under German groundwater assessment methodology, a default soil/soil-water partitioning coefficient data (K_d) is not provided, due to low mobility of Cd in groundwater [16] implying that using the DAF approach will result in an overestimate of groundwater concentration.

The soil/soil-water partitioning coefficient used in Equation 2 is pH-dependent. In the absence of site-specific soil pH, the default recommended soil pH of 6.8 was used in this analysis, corresponding to a Cd soil/soil-water partitioning coefficient of 75 L/kg. The latter coefficient ranges from 17 L/kg at soil pH of 5 to 4,300 L/kg at soil pH of 8 [11]. The equilibrium concentration of Cd in impacted soil is proportional to the soil/soil-water partitioning coefficient (Eqn. 2). Therefore, under acidic soils, the exposure point concentration in soil may be up to a factor of 4.4 lower than the concentration estimated in Table 2. For alkaline soils, the exposure point concentration in soil may be up to a factor of 57 higher than the concentration estimated in Table 2. However, because the soil exposure point concentrations in Table 2 are over two orders of magnitude below screening levels, potential health risks from exposure to soil are highly unlikely under varying soil pH.

The number of building downspouts (25) is based on the commercial building roof area being 25 times larger than a standard residential building with one downspout. The number of downspouts affects the impacted soil area (parameter IA in Eqn. 3), with each downspout discharging onto 1 m^2 of ground surface area. With additional downspouts, the soil exposure point concentration estimated with Equation 3 would increase proportionally. However, because the soil exposure point concentrations in Table 2 are over two orders of magnitude below screening levels, potential health risks from exposure to soil are highly unlikely under variations in the number of building downspouts.

Another screening level assumption is the module breakage rate. Product return statistics have been obtained in the 2011 fourth quarter from First Solar's warranty manager evaluating global warranty trends (J. Sokol, First Solar, Perrysburg, Ohio, USA, personal communication), including five years of actual performance data with extrapolations to later years of product life, based on an observed decline in breakage rate after the installation and initial operating period. Module breakage is rare, occurring in approximately 1% of modules over the 25-year warranty operating life, including the shipping and installation period. Of these breakages, over one-third occurs during shipping and installation and are removed for takeback and recycling. In addition, a proportion of broken modules have only chipped glass that does not affect the CdTe semiconductor layer. These two considerations considerably reduce the relevant breakage rate for modules that may be subject to leaching by rainfall. Nevertheless in this analysis, a conservative breakage rate of 1% over a 25-year life (0.04%/year) is applied.

The screening level approach used in this evaluation considers each exposure medium (soil, air, groundwater) separately. If an exposure point concentration for a chemical exceeds a screening level, the chemical is of potential concern to human health and requires further risk assessment. Conversely, if a screening level is not exceeded, it is highly unlikely that the chemical may pose a potential health risk in that exposure media. In addition to screening health risks for each exposure medium, cumulative risks across exposure media were considered using the exposure point concentrations in Table 2 in conjunction with U.S. EPA exposure assessment methodology [26,27] and the inhalation unit risk and oral reference dose for Cd (http://www.epa.gov/iris/subst/0141.htm). Across the exposure media of soil, air, and groundwater, cumulative risks and hazards are below one in one million and the hazard index of 1, respectively, as expected given that the media-specific exposure point concentrations are orders of magnitude below human health screening levels.

Overall, a worst case leaching scenario with screening level fate and transport modeling yields impacts to soil, air, and groundwater that are one to five orders of magnitude below human health screening levels in a California and southern

Germany exposure scenario. Potential exposures to Cd from rainwater leaching of broken modules in a commercial building scenario are highly unlikely to pose a potential health risk to on-site workers or off-site residents.

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Assessment of leaching tests for evaluating potential environmental impacts of PV module field breakage

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***Abstract* — Test methods from standard waste characterization leaching tests used in the U.S., Germany, and Japan were evaluated to determine if they can be used to help evaluate potential environmental impacts from PV field breakage. To assess the representativeness of leaching test methods, PV module breakage types were evaluated from warranty return data. Field breakages mainly consist of various types of stress and impact fractures in which modules remain largely intact with a number of glass fractures or cracks. By breaking modules into cm-scale pieces and tumbling them in solvent, waste characterization leaching tests can be more aggressive than PV field breakage conditions with regards to parameters such as fragment sample size, solvent, and treatment method. An alternative test method was previously used in Japan in which modules with a predetermined number of cracks were subjected to simulated rainwater. This approach is more representative of field conditions as modules are more likely to experience cracks under field conditions than to break into pieces.**

***Index Terms* —photovoltaic systems, environmental management, risk analysis**

I. INTRODUCTION

With global installed capacity reaching approximately 180 GW through 2014 [1], solar photovoltaics (PV) are making a significant contribution to new electricity supply in key markets around the world. By directly converting sunlight to electricity without emissions, solar PV can provide a sustainable alternative to conventional electricity generation. Development of utility-scale solar PV projects can require evaluation of a wide variety of potential environmental impacts, including impacts on biodiversity, land use, water resources, and human health [2][3]. Some stakeholders have raised concerns about the potential environmental impacts of PV modules due to the presence of environmentally sensitive materials, such as compounds of Pb, Cd, In, and Se. Under normal operation, PV modules do not pose a risk to human health or the environment, as the semiconductor layer is encapsulated between a layer of glass and a backsheet or a second layer of glass.

However, questions may arise with regards to non-routine events, namely broken modules subject to leaching by precipitation. Broken modules refer to modules with cracked glass or broken pieces which may result from extreme weather or human factors. In the case of thin film cadmium telluride (CdTe) PV modules, module breakage is rare, occurring in approximately 1% of modules over the 25-year warranty operating life (0.04%/yr) [4]. Of these breakages, over one-third occur during shipping and installation and are removed prior to plant operation. There is an observed decline in breakage rate after the installation and initial operating period (Fig. 1) [5]. In addition, a proportion of broken modules have only chipped glass that does not affect the semiconductor layer.

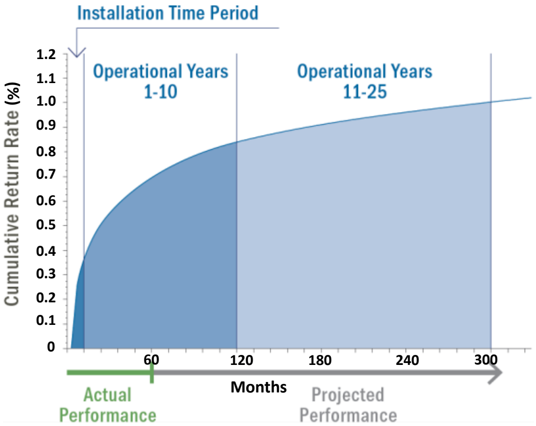

Fig. 1. Cumulative breakage rate as a function of months in service.

While rare, breakage followed by precipitation may potentially result in leaching of metals from modules and subsequent exposure in soil, air, or groundwater. Standard leaching tests could be used to try to evaluate the potential environmental impacts of broken PV modules. However, leaching tests have typically been designed for one of two objectives: identification of contents or waste characterization for landfill disposal.

Contents testing determines the total concentration of each target analyte in a sample. In the case of identifying metal constituents in PV modules, contents testing typically consists of acid digestion followed by spectrometry [6]. Samples are prepared by crushing module pieces to a powder (mm scale or smaller) and digesting with repeated additions of strong acid and oxidizing agent. The extracted metals are subsequently measured with methods such as inductively coupled plasma-atomic emission spectrometry. Waste characterization testing evaluates the soluble portion of analytes in a sample using conditions representative of a landfill. Test methods evaluate small (cm scale) fragments to account for potential crushing of waste by landfill equipment.

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TABLE I

SUMMARY OF WASTE CHARACTERIZATION LEACHING TEST METHODS AND RESULTS FOR PV MODULES IN THE U.S., GERMANY, AND JAPAN

Geography		**United States [7]**	**Germany [8]**	**Japan [9]**
Leaching Test		U.S. EPA Method 1311 (TCLP)	DIN EN 12457-4:01-03	Ministry of Environment Notice 13/JIS K 0102:2013 method (JLT-13)
Sample size (cm)		1	1	0.5
Solvent		Sodium acetate/ acetic acid (pH 2.88 for alkaline waste; pH 4.93 for neutral to acidic waste)	Distilled water	Distilled water
Liquid:Solid Ratio		20:1	10:1	10:1
Treatment Method		End-over-end agitation (30±2 rotations per minute)	End-over-end agitation (5 rotations per minute)	End-over-end agitation (200 rotations per minute)
Test Temperature		23±2˚C	20˚C	20˚C
Test Duration		18±2 hr	24 hr	6 hr
Leachate Cd Concentration (mg/L)	CdTe PV	0.22	0.0016 - 0.0040	0.10-0.13
	c-Si PV	Non-detect (<0.1)	-	Non-detect (<0.01)
	Limit	1	0.1	0.3
Leachate Pb Concentration (mg/L)	CdTe PV	Non-detect (<0.1)	-	Non-detect (<0.01)
	c-Si PV	3-11	-	Non-detect (<0.01) - 0.90
	Limit	5	-	0.3

The purpose of this study is to evaluate whether standard leaching tests can be used to help evaluate potential environmental impacts from PV field breakage. The focus is on waste characterization leaching tests, because contents testing provides data on the total quantity of metals but not their availability under field conditions. In this study, field breakage conditions are compared with waste characterization leaching test methods to determine the representativeness of the methods.

II. METHODS

Test methods from standard waste characterization leaching tests used in the U.S., Germany, and Japan were evaluated with regards to key parameters such as fragment sample size, solvent, and treatment method. To assess the representativeness of these parameters, product return data were obtained over nine years of field deployment of thin film CdTe PV modules. Module breakage types were analyzed, corresponding to standard categories recorded during warranty returns, including various types of stress and impact fractures. Data from the U.S. National Atmospheric Deposition Program were analyzed to assess the range of acidity typically present in rainfall, for comparison with solvents used in leaching tests.

III. RESULTS

Key test method parameters from leaching tests in the U.S., Germany, and Japan are presented in Table 1. These parameters are evaluated with regard to their relevance to PV field breakage conditions.

Sample size

The leaching test sample size in Table 1 ranges from 0.5-1 cm. In contrast, when PV modules break in the field, they tend to fracture (Fig. 2), rather than break into distinct pieces, due to the industrial laminate that encapsulates the module. Based on warranty return data over 9 years of service, field breakages largely consist of various types of stress and impact fractures (Fig. 3), not cm-scale fragments. Impact fractures are caused by external projectiles such as hail. Stress fractures are caused by dynamic/static loads such as wind, snow, and ice, or by thermal or physical propagation of undetected microscopic defects resulting from installation and handling damage. Module breakages can also occur at the attachment point due to improper clamping. Additional review of failure modes for PV modules is available from the International Energy Agency [10].

Fig. 2. PV module with fractured glass (impact, edge breakage).

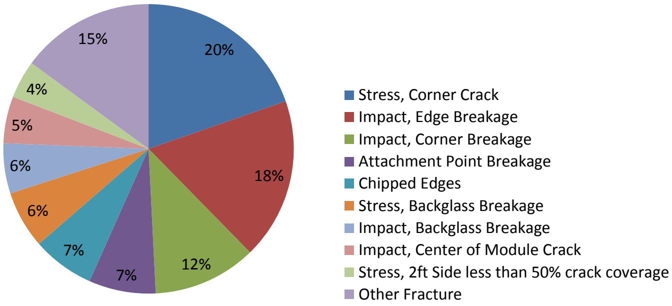

Fig. 3. PV module breakage types from warranty return data for modules put into operation (1-113 months in service).

Solvent

Solvents used in leaching tests range from organic acids to distilled water (Table 1). Organic acids are used to represent mixed waste disposal conditions in which organic acids are produced through fermentation of organic waste. Mixed waste conditions do not exist in PV field breakage. Based on data from the U.S. National Atmospheric Deposition Program [11], the average annual pH of rainwater in the U.S. ranges from approximately 4.7-6.7 (Fig. 4), which is less acidic than the range of 2.88-4.93 used in the TCLP test.

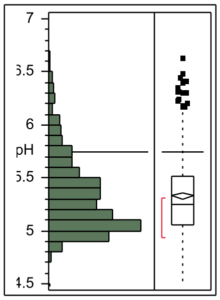

Fig. 4. Average annual rainfall pH in the U.S. (2011-2013) [11].

Treatment method

The sample treatment method of immersion in solvent and rapid end-over-end agitation (Table 1) is designed to accelerate the aging of the sample in order to allow a 6-24 hr test to represent long-term leaching potential in landfill conditions. However, there is an incentive to detect and remove non-performing modules, rather than leave them indefinitely in the field, which reduces the potential for long-term leaching. Broken modules can be detected though routine inspections of modules or power output monitoring. The latter may include diagnostic comparison of actual to expected performance or comparison of co-located arrays to identify low performance areas and modules that are nonfunctioning potentially due to breakage [4].

IV. DISCUSSION

The evaluation of test methods indicates that waste characterization leaching tests can be more aggressive than PV field breakage conditions with regards to parameters such as fragment sample size, solvent, and treatment method. In order to provide further bounds on worst-case leaching potential from field breakage, data from two additional cases are also discussed. Data are presented from previous leaching tests of the raw semiconductor material CdTe, and from intentional crushing of PV modules by a heavy-duty landfill compactor.

CdTe has a very low solubility product in water ($K_{sp} = 9.5\times10^{-35}$) derived using Outotec HSC Chemistry software (V. 7.0) and experimental water solubility testing following OECD Test Guideline 105 [12]. The CdTe K_{sp} corresponds to an equilibrium Cd concentration in water of 9.7×10^{-18} mol/L based on (1)-(3), or 1.1×10^{-12} mg/L given the molecular weight of Cd (112.414 g/mol). The stoichiometric balance in (2) is based on the high purity (99.999%) of semiconductor grade CdTe.

$$K_{sp} = [Cd^{2+}][Te^{2-}] \tag{1}$$

$$[Cd^{2+}] = [Te^{2-}] \tag{2}$$

$$[Cd^{2+}] = \sqrt{K_{sp}} \tag{3}$$

TABLE II

SUMMARY OF LEACHING TEST METHODS AND RESULTS ON THE RAW SEMICONDUCTOR MATERIAL CDTE*

	TCLP[a] [13]		**WET[b] [13]**		**Dissolution [13]**	**Dissolution [14][15]**	**Bio-elution [14][16]**
Sample size (µm)	63-125		63-125		63-125	92-262	74-<100
Solvent	Acetic acid, sodium hydroxide (pH 4.93)		Citric acid, sodium hydroxide (pH 5)		Hydrochloric acid, sodium hydroxide (pH 3.5)	CO_2-buffered water (pH 6)	Hydrochloric acid (pH 1.5)
Headspace	N_2	Ambient air	N_2	Ambient air	Ambient air	0.5% CO_2-in-air	Ambient air
Temperature (˚C)	Room		Room		30	20-23	36-38
Treatment method	Agitation at 21 rpm for 18 hr		Agitation at 21 rpm for 48 hr		Agitation at 120 rpm for 72-600 hr	Agitation at 100 rpm for 168-672 hr	Agitation at 150 rpm for 1 hr, then resting for 1 hr
% Cd release (w/w)	0.58%	6.4%	0.56%	5.3%	≤3.6%	3.2 - 4.1%	2.3%

*See Discussion for interpretation for CdTe-containing devices

a – U.S. EPA Method 1311 Toxicity Characteristic Leaching Procedure

b - Waste Extraction Test

Given acidic conditions ranging from pH 1.5 to 6, leaching tests on the raw semiconductor material CdTe indicate a range of approximately 0.56% to 6.4% (w/w) solubility of Cd content in CdTe (Table 2). This range is nearly an order of magnitude lower than assumed in a previous worst-case environmental impact assessment [17], where the latter is based on modified availability testing that is more aggressive than standard waste characterization leaching tests and field breakage conditions.

Note that both the material tested and some of the test methods in Table 1 differ from those in Table 2. Table 1 provides leaching test methods and results for PV modules, whereas Table 2 provides leaching test methods and results for the raw semiconductor material (CdTe). Table 1 provides leaching test methods for waste characterization for landfill disposal. Table 2 provides leaching test methods for both waste characterization (TCLP and WET tests) and for evaluating solubility under a wider range of conditions (bioelution and long-term dissolution tests). The TCLP test is the federal U.S. waste characterization test whereas the WET test is the waste characterization test used in the State of California. For each of the TCLP and WET test methods in Table 2, two solubility results are provided corresponding to aerobic conditions (ambient air headspace) and anoxic conditions (N_2 headspace), with lower solubility observed under anoxic conditions.

Additional data is required to use the evaluation of the raw semiconductor material CdTe in Table 2 to try to understand potential leaching behavior of CdTe-containing devices. For example, CdTe PV modules contain approximately 6 g Cd content per 12 kg device [4] or 0.05% Cd content by mass, and the leaching potential is further limited by the monolithic glass-adhesive laminate-glass structure of the device that encapsulates the semiconductor material.

The potential leaching behavior of CdTe PV modules in a standard 1 L TCLP extraction fluid can be estimated using (4).

$$C_{Cd} = \frac{M_{EF} \times SL \times CO_{Cd} \times L_{Cd}}{AF_{EN} \times V_{EF}} \qquad (4)$$

where,

C_{Cd}: TCLP Cd leachate concentration (mg/L),

M_{EF}: mass of extraction fluid (10^6 mg),

SL: TCLP solid-liquid ratio (1/20),

CO_{Cd}: Module Cd content (0.05%),

L_{Cd}: leaching potential of Cd content (6.4%),

AF_{EN}: adjustment factor to account for raw semiconductor material encapsulation in glass-adhesive laminate-glass structure, and

V_{EF}: volume of extraction fluid (1 L).

By taking the measured value of C_{Cd} from TCLP testing in Table 1 (0.22 mg/L), the adjustment factor (AF_{EN}) is estimated as ~7. In other words, in addition to the low mass concentration and solubility of the raw CdTe semiconductor material, the glass-adhesive laminate-glass encapsulation is estimated to further reduce solubility under standard TCLP conditions by nearly an order of magnitude, with the TCLP conditions already aggressive compared with field breakage.

In addition to the raw semiconductor material evaluation, a hypothetical case that provides perspective on field breakage is the intentional crushing of PV modules in a landfill. This is a hypothetical case because tractor compaction cannot take place in an operating PV array; however, even under six passes over the PV modules by a heavy-duty landfill compactor (Fig. 5), PV modules remain largely intact (Fig. 6) with the vast majority of pieces larger than the sample size

(0.5-1 cm) used in waste characterization leaching tests (Fig. 7) [18].

Fig. 5. Aljon model 91K compactor used to crush PV modules in a Municipal Solid Waste Landfill in the State of Arizona, USA.

Fig. 6. Compactor foot punch-out of a PV module crushed in a Municipal Solid Waste Landfill in the State of Arizona, USA.

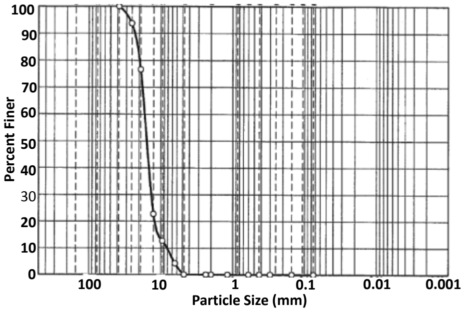

Fig. 7. Fragment size distribution of a PV module crushed in a Municipal Solid Waste Landfill in the State of Arizona, USA.

In testing of early generation PV modules, the New Energy and Industrial Technology Development Organization (NEDO) in Japan commissioned the study of leaching potential of thin film CdTe PV modules using methods more representative of field breakage conditions [19]. Instead of breaking modules into cm-scale pieces and tumbling in solvent, the testing subjected intact modules with 1 to 5 cracks to a quantity of simulated acid rain (pH 5) equivalent to 40 days of average rainfall. This approach is more representative of field conditions as modules are more likely to experience cracks under field conditions then to break into pieces.

Instead of developing leaching tests that more closely resemble field breakage conditions, some recent investigations have modified test parameters to be even more aggressive than standard waste characterization tests [20-22]. The use of finely ground samples and multiple extraction cycles in these investigations mimics the recycling process for PV modules [23] more closely than any environmental conditions, where the recycling process has the explicit objective to separate and then recover and reuse metals from end-of-life modules. As with contents testing, such worst case leaching tests provide data on the total quantity of metals but not their availability under realistic field conditions.

In addition, leaching tests are used to estimate potential chemical emissions; however, emissions are not equivalent to impacts. In order to conduct environmental impact analysis, fate and transport analysis is further needed to evaluate the chemical transformations and dispersion of chemicals in the environment in moving from the point of emissions to the point of exposure (or impact) [4]. Other factors such as breakage rate and exposure factors (frequency, type, and duration of exposure to impacted soil/water/air) also have to be accounted for to estimate potential impacts to human health and the environment.

V. CONCLUSION

Leaching tests used to evaluate the potential health and environmental impacts of rainwater leaching of broken PV modules need to reflect realistic PV field conditions. The evaluation of test methods indicates that waste characterization leaching tests can be more aggressive than PV field breakage conditions with regards to parameters such as sample size, solvent, and treatment method. Some recent worst case leaching tests are even more aggressive than waste characterization leaching tests and more closely resemble the PV recycling process or contents testing than realistic field conditions. An alternative test method was previously used in Japan in which modules with a predetermined number of cracks were subjected to simulated rainwater. This approach is more representative of field conditions as modules are more likely to experience cracks under field conditions then to break into pieces.

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Future trends in soil cadmium concentration under current cadmium fluxes to European agricultural soils

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HIGHLIGHTS

- The mass balance of cadmium in European agricultural soils was updated
- Lower-fertiliser use and lower cadmium deposition have lowered cadmium additions
- Cadmium concentrations in EU topsoils are predicted to decrease on the long term

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ABSTRACT

The gradual increase of soil cadmium concentrations in European soils during the 20th century has prompted environmental legislation to limit soil cadmium (Cd) accumulation. Mass balances (input–output) reflecting the period 1980–1995 predicted larger Cd inputs via phosphate (P) fertilizers and atmospheric deposition than outputs via crop uptake and leaching. This study updates the Cd mass balance for the agricultural top soils of EU-27 + Norway (EU-27 + 1). Over the past 15 years, the use of P fertilizers in the EU-27 + 1 has decreased by 40%. The current mean atmospheric deposition of Cd in EU is 0.35 g Cd ha^{-1} yr^{-1}, this is strikingly smaller than values used in the previous EU mass balances (~3 g Cd ha^{-1} yr^{-1}). Leaching of Cd was estimated with most recent data of soil solution Cd concentrations in 151 soils, which cover the range of European soil properties. No significant time trends were found in the data of net applications of Cd via manure, compost, sludge and lime, all being small sources of Cd at a large scale. Modelling of the future long-term changes in soil Cd concentrations in agricultural top soils under cereal or potato culture predicts soil Cd concentrations to decrease by 15% over the next 100 years in an average scenario, with decreasing trends in some scenarios being more prevalent than increasing trends in other scenarios. These Cd balances have reverted from the general positive balances estimated 10 or more years ago. Uncertainty analysis suggests that leaching is the most uncertain relative to other fluxes.

1. Introduction

Cadmium (Cd) is a toxic trace metal that can be a risk for human health and the environment due to its environmental bioavailability and relatively large toxicity. Cadmium exposure to the general population occurs mainly via smoking, followed by ingestion of Cd containing food (IPCS, 1992). The risks due to Cd have been given much attention since the discovery of the '*itai-itai*' disease in Japan. The biological half-life of Cd in humans is 15–20 years. This means that a rare consumption of a high Cd containing food item has less effect than the lifetime exposure of moderately contaminated food.

Cadmium concentrations in crops increase with increasing soil Cd concentrations, all other factors being constant (Eriksson et al., 1996; McLaughlin et al., 2011; Smolders et al., 2007). Therefore, managing the risk of exposure to Cd via food includes managing the soil Cd balance and avoiding excessive accumulation of Cd in soils through additional inputs. Analysis of archived soil samples from experimental stations in UK, France and Denmark revealed that soil Cd increased by factors 1.3–2.6 during the 19th and 20th century (Jones et al., 1987; Juste and Tauzin, 1986; Rothbaum et al., 1986; Tjell and Christensen, 1985). Archived wheat grain samples similarly revealed an increasing trend in Cd concentrations over the same period in some field trials (Andersson and Bingefors, 1985; Jones and Johnston, 1989).

The atmospheric deposition of Cd and applications of phosphate (P) fertilizers, lime, sewage sludge or manure contaminated with Cd are net sources of Cd. These may exceed the leaching losses and removal of Cd with the harvested crop (crop offtake). Several mass balances for Cd have been used to derive trends in soil Cd in Europe. All predicted a net accumulation of soil Cd (Hellstrand and Landner, 1998; Hutton, 1983; Kiene, 1999; Moolenaar and Lexmond, 1998; Tjell and Christensen, 1992). The average soil Cd concentrations in European soils is about

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0.3 mg Cd kg^{-1}, equivalent to about 900 g Cd ha^{-1} in the plough layer (Smolders and Mertens, 2013). Between 1980 and 1995, the annual net input fluxes of Cd in European soils were estimated to range between 1 to 10 g Cd ha^{-1}, indicating that annual fluxes are much smaller than the total Cd stock in soils. In 2003, a proposal has been made in Europe to set limits on Cd in P fertilizers based on the stand-still principle, i.e. a proposal to set limits on Cd in fertilizers that would not lead to a long-term accumulation of Cd in European agricultural soils (CSTEE, 2002; DG Enterprise, 2003). That proposal has never been adopted into EU-wide regulations. Since that assessment in 2003, important emission controls have been taken to reduce atmospheric deposition of heavy metals to soils. Pacyna et al. (2009) concluded that the anthropogenic Cd emissions reduced considerably over the past 30 years. Next to a true reduction in Cd emission (and thus also Cd deposition), the current measurements of Cd concentration in precipitation with ICP-MS (inductively coupled plasma mass spectrometry) allows determination of lower Cd concentrations compared to previous methods (graphite furnace atomic absorption spectrometry or GF-AAS). Hence, the actual Cd deposition rates can now be estimated with greater accuracy compared to 1990s–2000s. In addition, trend analyses show a decreasing trend in P fertilizer consumption in Europe.

Leaching of Cd from soil is likely the most difficult flux to estimate in the mass balance since in situ annual flux data are not available at a large scale. Soil solution Cd concentrations can be estimated from solid-soil solution partitioning, expressed with a partitioning or distribution coefficient (K_D) of Cd in soils. This K_D value is most often related to basic soil properties (e.g. soil pH, organic carbon content, and total soil Cd concentration) (Groenenberg et al., 2010). By compiling different data sets with reliable K_D measurements, robust relationships can be deducted, which in turn allows a more reliable estimation of the Cd losses through leaching.

This study was set up to update the inventory of Cd inputs to agricultural soils in EU 27 + Norway (EU27 + 1) with recent data on atmospheric deposition, P fertilizers, sludge, lime and manure applications for soils used for arable production. The dietary intake of Cd mainly occurs via cereals and potatoes (Smolders and Mertens, 2013). Therefore, soils under cereal and potato production are used as cropping systems. The Cd output through leaching is estimated using an updated K_D model derived from coupled data on soil solution Cd concentrations and total soil Cd concentrations available from different studies. Model analysis is used to predict long-term (100 years) changes in Cd concentrations in top soils. In this study, the relative importance of the Cd inputs and outputs is estimated at European scale and compared with previous estimations. Expected long-term changes in soil Cd are estimated for the European average as well as for different regional scenarios representative for Europe. Finally, a sensitivity analysis is included.

2. The Cd mass balance: model description

The long-term changes in soil Cd concentrations were calculated from the annual input–output and the existing Cd concentration in European soils. The Cd concentration of the top soil at year i ($[Cd]_{soil,\ i}$, in mg Cd kg^{-1} soil) is calculated from the net Cd balance (i.e. input–output, in g Cd ha^{-1} yr^{-1}) in year (i − 1) and the total soil concentration in year (i − 1) ($[Cd]_{soil,\ i-1}$, in mg Cd kg^{-1} soil):

$$[Cd]_{soil,i} = [Cd]_{soil,i-1} + \frac{input-output}{W_{soil}} \tag{1}$$

with W_{soil} as the soil weight in the plough layer (tonnes ha^{-1}). Using a bulk density of 1200 kg m^{-3} and a soil depth of 25 cm, this corresponds to W_{soil} = 3000 tonnes soil ha^{-1}. It was further assumed that the soil is homogeneously mixed without vertical variation of the soil properties in the top soil and that water transport is only in the vertical direction by prop flow. Preferential or bypass flow of water and thus Cd is not considered in this model. The impact of surface runoff and erosion was not considered as a loss of Cd, as erosion is merely a redistribution of Cd within the landscape.

This mass balance is made for the entire EU-27 + 1. For obtaining the EU average change, the EU average for the different parameters was used. Next to this, a full factorial analysis was performed, in which different model parameters (soil pH, % organic carbon, atmospheric deposition, P application, crop properties, leaching rate) are combined with each other. Although some combinations or scenarios are not equally important as others, this full factorial analysis allows quantifying the uncertainty on our estimated average. Furthermore, we have selected some regional (country) scenarios: Germany for Central Europe, United Kingdom for Western Europe, Spain for the Mediterranean region and Czech Republic for Eastern Europe.

The use of average balances, rather than local balances is preferred as the average situation controls the exposure of Cd to the general population. Cumulative lifetime consumption of staple crops, cereal and potato products is only exceptionally derived from a single location. The chronic (lifetime) Cd intake determines the risk of Cd for humans rather than the single high intake events (Järup et al., 1998; Smolders and Mertens, 2013). This justifies the use of generic mass balances instead of site-specific approach. Logically, a local mass balance is defensible when evaluating the likelihood that locally grown crops will exceed a food limit. Since a risk assessment is outside the scope here, we compare the current gross balances with similar balances made before for EU. In following sections the underlying assumptions of the model are explained in more detail.

2.1. Soil Cd concentrations of arable land in Europe

The soil Cd concentration at time t = 0 has a major impact on the predicted future Cd concentrations. Total soil Cd concentrations typically range between 0.1 and 1 mg Cd kg^{-1} (Smolders and Mertens, 2013). A large scale sampling programme by FOREGS in 2006, in which total metal concentrations are measured after a hot acid digestion, shows that the average Cd concentration in Europe is 0.28 mg Cd kg^{-1} with a standard deviation of about 0.24 mg Cd kg^{-1}. This is in close correspondence with country averages presented in the European risk assessment report (EU, 2007). For modelling the future soil Cd concentrations this average value, 0.28 mg Cd $(kg\ soil)^{-1}$, is used. For the country assessment, country specific data was used when available.

2.2. Atmospheric deposition

Cadmium is emitted to the atmosphere from anthropogenic and natural sources. The anthropogenic sources of Cd include industrial and small combustion, flue gas of industrial processes, waste incineration and others (EMEP, 2012). Emission trend analysis by Pacyna et al. (2007) shows that the highest emissions of Cd in Europe were around the mid-1960s when the production of non-ferrous metals (Zn smelters) was growing rapidly. Current Cd emissions are lower by a factor 5 since mid-1960s or by a factor 3 since 1985. From the mid-1970s on, the flue gasses were more filtered which resulted in a decline in Cd emissions.

Trace metals are included in EMEP's atmospheric monitoring programme since 1999, but earlier data have also been collected for a few sites. In 2010, a total of 33 sites are measuring trace metals in both air and precipitation in EU27 + 1 (EMEP, 2012). On these monitoring sites, two sampling methods are used, i.e. bulk collectors and wet-only collectors, although the wet-only collectors are being recommended in the EMEP manual. With wet-only collectors, the sampler is only opened during rain events. The main advantage of the wet-only collectors over the bulk collectors (always open) is that re-suspended Cd, which was first deposited elsewhere, is not accounted for in the measurements. After sampling, the concentrations are measured preferentially by the ICP-MS method which allows determination of Cd concentrations down to 0.01 μg Cd L^{-1}. Nevertheless, some countries still

Table 1
Atmospheric Cd deposition rates (g Cd ha^{-1} $year^{-1}$) in selected European countries (EU27 + 1) in 2010.

Country	Bulk sampler	Wet only collector
Belgium		0.2
Czech Republic	0.4	0.4
Denmark	0.2–0.8	
Estonia	0.5–1.2	
Finland	0.2–0.5	
France	0.3	0.1–0.2
Germany		0.2–0.3
Hungary		0.4
Latvia		0.4–0.6
Lithuania	0.4	
Netherlands		0.1–0.2
Poland		0.3–0.4
Slovakia		0.5–1.0
Slovenia	0.3	
Spain		0.3
Sweden		0.1–0.6
United Kingdom	0.1	
Norway	0.2–0.7	
EU-27 + 1 (mean and standard deviation)[a]	0.35 (0.21)	

Data is based on Cd measurements of the EMEP/CEIP monitoring sites.

[a] The range was averaged to obtain a country mean and means of all country means were then calculated.

use ICP-OES or even GF-AAS, which may yield at least tenfold larger detection limits. For each monitoring station, information is available for each rain event or for a fixed period. Based on the precipitation (mm) recorded and the Cd concentration in the rainwater (μg Cd L^{-1}) measured per rain event, the Cd deposition (mg Cd m^{-2}) can be calculated. By summing all rain events and converting to g Cd ha^{-1}, we obtained an estimate for total Cd deposition per monitoring station. The Cd deposition ranges between 0.1 and 1.0 g Cd ha^{-1} (Table 1), with an average of 0.35 g Cd ha^{-1} yr^{-1} and standard deviation of 0.21 g Cd ha^{-1} yr^{-1}. Next to the average deposition rate, the scenario of zero atmospheric deposition and a realistic worst case of 0.7 g Cd ha^{-1} yr^{-1} were also used in the full factorial analysis.

For comparison, total annual Cd emissions reported by EMEP and in the ESPREME project (espreme.ier.uni-stuttgart.de; EU 6th framework programme) divided by the total surface of Europe yield an average atmospheric deposition ranging between 0.2 and 0.6 g Cd ha^{-1} yr^{-1}, which is in close correspondence with measured Cd deposition.

The measured Cd deposition has decreased by a factor 5 or more in several monitoring stations, such as in Germany (EMEP/CEIP, 2012a). The Cd concentrations in mosses in Europe, indicating Cd deposition, decreased with a factor 1.3 to 4 depending on the country between 1990 and 2005 (Harmens et al., 2012). The previous Cd mass balances made for European soils (CSTEE, 2002; EU, 2007; Hutton and Symon, 1986; Jensen and Bro-Rasmussen, 1992; Nicholson et al., 2003) have assumed average Cd deposition fluxes that were up to 8 times larger than current means. The decreasing trends in measured Cd deposition (EMEP/CEIP, 2012b) are relatively more pronounced than the recent trends in estimated emissions (Pacyna et al., 2007; Pacyna et al., 2009). This is likely due to the lower detection limits with current analytical instruments (ICP-MS vs. GF-AAS) and due to the conversion of bulk samplers to wet only collectors.

2.3. Inputs from P fertilizers

Phosphate fertilizers, among all mineral fertilizers, are generally the major source of Cd in agricultural soils (Smolders and Mertens, 2013). The Cd input via fertilizers depends on the consumption of P fertilizers on one hand, and on the Cd:P_2O_5 ratio in the fertilizer. Detailed statistics on P fertilizer use (kg P_2O_5 ha^{-1}) in each EU 27 + 1 member state were provided by Fertilizers Europe (2011). The actual consumption is calculated by country experts, based on sales of fertilizers, the cropping area and the nutrient application rates for each crop. The current European average consumption of P_2O_5 on arable land is 22 kg P_2O_5 ha^{-1}, with an average P application of 21 kg P_2O_5 ha^{-1} for cereals and 45 kg P_2O_5 ha^{-1} for potato (Fertilizers Europe, 2011). The Cd concentration of P fertilizers (pure or blended) used in Europe were extensively investigated by Nziguheba and Smolders (2008). This study compiled the Cd concentrations of 196 samples of P fertilizer collected in Europe (EU-15). The Cd concentrations ranged from <0.1 to 120 mg Cd $(kg\ P_2O_5)^{-1}$, with a mean of 36 mg Cd $(kg\ P_2O_5)^{-1}$. Using this mean Cd concentration for P fertilizers, the annual input of Cd to arable soils is estimated to be about 0.8 g Cd ha^{-1} yr^{-1} for the European average consumption, also 0.8 g Cd ha^{-1} yr^{-1} for cereal-based production, 1.6 g ha^{-1} yr^{-1} for potato production and for potato (1 year)-cereal (2 years) rotations a Cd input of 1.1 g Cd ha^{-1} yr^{-1} is calculated. Country averages of Cd inputs to cereals through P fertilizers for different European scenarios are shown in Table 6.

Since 1980, the consumption of P fertilizers in Europe (EU27 + 1) has decreased by a factor four (Fig. 1). The actual Cd input via fertilizers has decreased mostly due to the reduction in P fertilizers use. For example, at the average use for arable land of 36 kg P_2O_5 ha^{-1} in 2001, the Cd input was 1.3 g Cd ha^{-1} yr^{-1}. Previous Cd mass balances estimated Cd addition rates via fertilizers between 0.5 and 4.4 g Cd ha^{-1} yr^{-1} (Alloway and Steinnes, 1999; CSTEE, 2002; Hutton, 1983; Moolenaar and Lexmond, 1998; Nicholson et al., 2003). These larger estimates most likely reflect the larger use of P fertilizers in Europe 10 to 30 years ago (Table 7).

2.4. Inputs from manure, sludge and lime

Inputs from manure, sludge and lime are in general difficult to estimate since national statistics are limited in Europe.

The Cd application through manure ranges between 1.4 and 6.1 g Cd ha^{-1} yr^{-1}, when applied at an equivalent N rate of 250 kg N ha^{-1} yr^{-1} (Nicholson et al., 2003). Such high estimate is unlikely representing the average EU scenario, since manure is only locally the single N source to plants. More importantly, this major local source of Cd is not an important net source of Cd at large scale. A majority of Cd in manure is derived from animal feed that is produced in the same region. Hence, manure application recycles Cd that was previously taken by crops (see crop offtake). Logically, at field scale, net accumulations of Cd are possible where manure is applied, whilst net depletion is possible where the feed is produced. For these reasons, average Cd mass balances only consider the net input of Cd through manures as the Cd that comes from imported animal feed (Moolenaar and Lexmond, 1998).

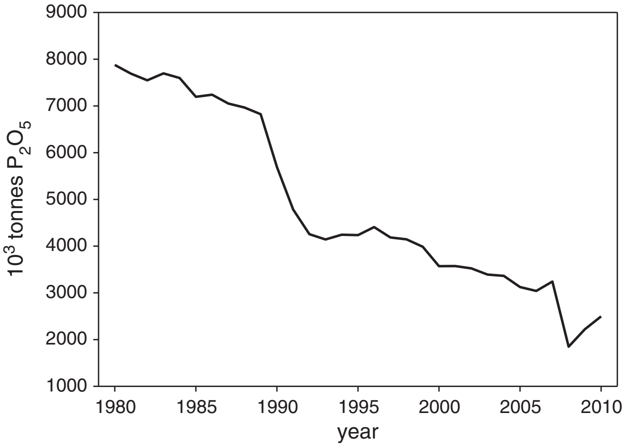

Fig. 1. Evolution of mineral P fertilizer consumption (10^3 tonnes P_2O_5) in the EU-27 member states + Norway from 1980 to 2010.
Source: IFA DATA (2012).

We assume that cereals are the main constituent for animal feed and we used typical grain Cd concentrations for calculations (Eriksson et al., 1996). We further assume that the resulting manure is evenly spread over the arable land in Europe (i.e. approximately 103×10^6 ha). In theory, Cd export via agricultural products (meat, milk, etc.) should also be subtracted, but that refinement was not done since the Cd input via manure is already a marginal one. Cereal grains contain on average 0.02 to 0.05 mg Cd (kg grain)$^{-1}$ (Smolders et al., 2007). In 2010, about 30×10^6 tonnes animal feed were imported into Europe. Based on these animal feed imports to EU-27, an annual Cd input of about 0.006–0.014 g Cd ha^{-1} yr^{-1} was estimated, yielding 0.01 g Cd ha^{-1} yr^{-1} for the European average in this assessment.

Hellstrand and Landner (1998) estimated that a total of 155 kg Cd is imported into Sweden through animal feeds. This corresponds to a Cd flux of 0.05 g Cd ha^{-1} yr^{-1} at the national level. The same Cd flux via manure was estimated by Moolenaar and Lexmond (1998) for Dutch mixed farming systems. In a recent mass balance study conducted for Sweden by Sternbeck et al. (2011), it was concluded that manure is of little importance for the accumulation of Cd in soil and was therefore not considered in their assessment.

For estimating Cd input through sludge application, Nicholson et al. (2003) based their calculations on N-requirements. If 250 kg N ha^{-1} is applied as sludge, this would lead to a Cd input of 19 g Cd ha^{-1} yr^{-1} with sludge containing 3.4 mg Cd (kg dry basis)$^{-1}$. Currently, the estimated EU average Cd content of sewage sludge is 1.8 mg Cd (kg dry basis)$^{-1}$, which leads to a twofold reduction compared to Nicholson et al. (2003). As with manure, such values unlikely represent the average situation, since such large amounts are only applied locally. Additionally, the application of sewage sludge to agricultural land is regulated differently among European Member States.

For above reasons, total Cd inputs to arable land via sludge application were calculated from the amounts of sludge used for agriculture (i.e. about 40% of total sludge production (Milieu et al., 2008)) and the average Cd concentration of the sludge produced in Europe (Table 2). Again it was assumed that all sludge is evenly spread over the arable land in EU 27 + 1 (i.e. 103×10^6 ha). Obviously, this results in an underestimation of local application rates, which can lead to locally high concentrations of Cd. The sludge application rates for some EU 27 + 1 countries and the Cd concentration of sludge used for fertilizer purposes are represented in Table 2.

On average, again assuming all sludge is evenly spread over arable land, the Cd inputs through sludge application are 0.05 g Cd ha^{-1} yr^{-1}. According to the country risk assessment studies submitted to the European Commission in 2000, country average fluxes were approximately 0.05 g Cd ha^{-1} yr^{-1} for Austria, Denmark, Belgium and Finland and were larger for The Netherlands and Germany: 0.2 g Cd ha^{-1} yr^{-1}.

In conclusion, sludge and manure application can be significant sources of Cd at a field level, but are no significant sources compared to fertilizer and atmospheric deposition inputs at the country or regional level (Table 6) with which the average trend of soil Cd should be calculated (de Meeûs et al., 2002). However, high application of sludge and/or manure could be a considerable input at parcel level and cause an increase in soil Cd concentrations. Local mass balances are therefore defensible when evaluating the likelihood that locally grown crops will exceed a food limit.

Only limited national data on application rates of lime and their Cd concentrations were found. We estimated the Cd input from liming using a Swedish risk assessment report (Sternbeck et al., 2011). Lime application rates of 100–150 kg CaO ha^{-1} yr^{-1} are recommended in Scandinavian countries to maintain pH at a good level. For their study, they used a long-term liming rate of 100 kg CaO ha^{-1} yr^{-1}. The average Cd concentration in lime currently available on Swedish markets is circa 0.4 mg Cd (kg CaO)$^{-1}$. This results in annual applications of 0.04 g Cd ha^{-1} yr^{-1}. In France, on total 2.16×10^9 kg of lime was applied to agricultural land (18.4×10^6 ha) in 2007 (Société chimique de France, 2007). This corresponds to an annual application of 120 kg CaO ha^{-1} yr^{-1}. If the Cd concentration is 0.35 (average of Sweden and UK), this is an input of 0.04 g Cd ha^{-1} yr^{-1}. For Germany, about 2×10^6 tonne CaO is spread over a total agricultural area of 17×10^6 ha, which is an application rate of 180 kg CaO ha^{-1} yr^{-1}. Given the large uncertainty on actual application rates, we assumed an average application rate of 250 kg CaO ha^{-1} yr^{-1} and a Cd concentration of 0.35 mg Cd (kg CaO)$^{-1}$ for our calculations. This results in an estimated Cd input of 0.09 g Cd ha^{-1} yr^{-1}. In strong contrast with our results, Nicholson et al. (2003) estimated that Cd inputs are 1.4 g Cd ha^{-1} yr^{-1}, assuming application rates of 4.8 tonnes of CaO ha^{-1} yr^{-1}. It is unlikely that such lime rate reflects the average sustained application rate in EU.

In total we estimate that 0.15 g Cd ha^{-1} yr^{-1} is added to agricultural soils in Europe via manure, sludge and lime applications.

2.5. Output via crop offtake

The Cd removed from soil through the harvested crop, by definition crop offtake, is the product of the yield of the harvested crop and its Cd concentration $[\mathrm{Cd}]_{\mathrm{crop}}$. The Cd taken up by plants depends on the soil properties and/or plant species. The soil properties typically influencing Cd uptake are the total Cd concentrations, soil pH and the soil organic matter (SOM) content. Increasing the soil Cd concentration increases the crop Cd all other factors being constant; however, the increase is somewhat less than proportional. Overall, regression models can be used to predict the relationship between soil properties and crop Cd concentration (McLaughlin et al., 2011). As shown below, crop offtake

Table 2
Cadmium inputs through sludge application in EU-27 + 1.

Country	Sludge application (kg ha^{-1})	Cd content (mg Cd kg^{-1})	Cd application (g Cd ha^{-1} yr^{-1})
Belgium	22.6	1.0–1.5	0.02–0.03
Bulgaria	3.5	1.6	0.01
Czech Republic	40.9	1.5	0.06
Denmark	17.8	1.0	0.02
Estonia	3.1	2.8	0.01
France	27.8	1.3	0.04
Germany	49.6	1.0	0.05
Lithuania	11.3	1.3	0.01
Spain	82.1	2.1	0.17
Sweden	21.4	0.9	0.02
United Kingdom	203.4	1.3	0.26
Nicholson et al. (2003)	40.0	3.4	0.14
Norway	73.8	0.4	0.03
EU27 + 1 average (without Spain and UK)	26.0	1.8	0.05 (0.03)

Total quantity of sludge spread on agricultural land (EUROSTAT, 2012) was used to calculate the sludge application rate (kg sludge ha^{-1}), assuming sludge is spread over the entire arable land. The Cd concentrations measured in the sludge (EC, 2001) were used to estimate the annual Cd application rates (g Cd ha^{-1} yr^{-1}) on arable land.

is small relative to the other Cd fluxes, hence a high precision in predicting Cd uptake is not required. To simplify the analysis, it is justified to assume that the Cd concentration in the crop changes proportionally with the soil Cd concentration (McLaughlin et al., 2011). This relationship is typically described by a transfer function (TF), i.e. the ratio of the Cd concentration in the crop and the soil Cd concentration, here both expressed a dry weight basis (mg (kg DM or dry soil)$^{-1}$):

$$\mathrm{TF} = \frac{[\mathrm{Cd}]_{\mathrm{crop}}}{[\mathrm{Cd}]_{\mathrm{soil}}}. \tag{2}$$

The Cd concentration in the crops can thus be derived from the soil Cd concentration. Several studies (Eriksson et al., 1996; Mench et al., 1997; Smolders et al., 2007; Wiersma et al., 1986) provide paired soil and crop data which allows the calculation of the TF. According to different studies, the TF for cereal grain ranges between 0.11 and 0.20 and is on average 0.14, whilst for potato an average TF of 0.06 was found (Table 3). The above-mentioned studies allow refining the assessment by including effects on soil properties, e.g. soil pH or total soil Cd, on the TF. As will be shown below, this hardly affects the soil balance. Existing regression models show that the $[\mathrm{Cd}]_{\mathrm{crop}}/[\mathrm{Cd}]_{\mathrm{soil}}$ ratio of winter wheat decreases less than 20% by increasing soil Cd from 0.2 to 0.6 mg Cd kg^{-1} (Eriksson et al., 1996). This justifies the use of the linear TF concept within the relevant Cd concentration range.

The European average yield for cereals is 5.1 tonnes grain per ha and 25.9 tonnes potato tubers per ha (Fertilizers Europe, 2011). At the average soil Cd concentration of 0.28 mg Cd kg^{-1}, this results in a crop offtake of 0.2 g Cd ha^{-1} yr^{-1} for cereals, 0.44 g Cd ha^{-1} yr^{-1} for potatoes and 0.38 g Cd ha^{-1} yr^{-1} for the rotation cereals (2 years) and potatoes (1 year).

2.6. Output via leaching

Leaching (g ha^{-1} yr^{-1}) represents an outflow of Cd from the top soil. There are different models predicting the vertical leaching of Cd, taking into account the retardation, flow rate, vertical dispersion, vertical heterogeneity in Cd binding properties and climatic data (e.g. Streck and Richter, 1997). Such information is not available at a large scale and mass balance approaches typically simplify the calculation by estimating it from the precipitation excess (F; m yr^{-1}) and the dissolved Cd concentration in the soil solution or pore water ($[\mathrm{Cd}]_{\mathrm{solution}}$; mg Cd L^{-1}) (Eq. (3)):

$$\mathrm{Leaching} = 10\ 000\ \ \mathrm{F}\ \ [\mathrm{Cd}]_{\mathrm{solution}}. \tag{3}$$

The average precipitation excess in Europe is estimated to be 0.2 m yr^{-1}. For the Mediterranean region this can be reduced to 0.05 m yr^{-1} and for regions with high rainfall a precipitation excess of 0.3 m yr^{-1} was used.

Table 3
The Cd soil–plant transfer factors (TFs) for cereals (wheat) grown in selected agricultural soils.

Crop	Country	$[\mathrm{Cd}]_{\mathrm{crop}}$ µg Cd (kg fresh weight)$^{-1}$	$[\mathrm{Cd}]_{\mathrm{soil}}$ µg Cd kg^{-1}	TF
Wheat grain	UK	38 (dry weight basis)	700	0.055
	France	58	435	0.11
	The Netherlands	60	400	0.15
	Sweden	40–69	270–420	0.14–0.20
	Germany	56	440	0.13
	Average	57		0.14
Potato	Sweden	10	270	0.04
	The Netherlands	30	400	0.08
	Germany	30	440	0.07
	Average	23		0.06

The TFs are calculated as the ratio of $[\mathrm{Cd}]_{\mathrm{crop}}$ and $[\mathrm{Cd}]_{\mathrm{soil}}$ (Eq. (1)). For more information on original references, we refer to the EU (2007).

The pore water Cd concentrations change almost proportionally with total soil Cd (keeping all other parameters constant). The $\mathrm{K_D}$ value (L kg^{-1}) represents partitioning of Cd between the solid phase $[\mathrm{Cd}]_{\mathrm{soil}}$ and solution phase or pore water (water held in pore space between soil particles), $[\mathrm{Cd}]_{\mathrm{solution}}$:

$$\mathrm{K_D} = \frac{[\mathrm{Cd}]_{\mathrm{soil}}}{[\mathrm{Cd}]_{\mathrm{solution}}}. \tag{4}$$

The Cd concentrations in European agricultural soils are typically <1 mg Cd kg^{-1}, concentrations at which sorption is linear (Christensen, 1984).

Different empirical regression models for predicting $\mathrm{K_D}$ values in soils from soil properties are in use (Degryse et al., 2009). In these models, log $\mathrm{K_D}$ values measured on a set of soils are related to a range of soil properties, for example:

$$\log\ \mathrm{K_D} = \mathrm{a} + \mathrm{b}\ \ \mathrm{pH_{CaCl2}} + \mathrm{c}\ \ \log(\mathrm{OC}) \tag{5}$$

in which OC is the percentage of organic carbon in a soil and $\mathrm{pH_{CaCl2}}$ is the soil pH measured in 0.01 M $\mathrm{CaCl_2}$. Soil pH determines the $\mathrm{K_D}$ most sensitively (Degryse et al., 2009).

Paired measurements of Cd in soil solution and Cd in soil were recently collected from previous studies conducted on European soils (Degryse et al., 2009) and these were complemented with some additional studies (Table 4). When $\mathrm{pH_{H2O}}$ was available a conversion was made to reflect $\mathrm{pH_{CaCl2}}$. We set selection criteria on these data. First, total soil Cd concentrations were required rather than a fraction of that (e.g. labile soil Cd concentrations) since the soil mass balance described below predicts the changes in total soil Cd only. Second, the determination of the Cd concentration in the solution phase is critical. In situ soil solution or pore water measurements should be used for predicting in situ migration of Cd through soils (Degryse et al., 2009). With in situ measurements the ionic strength and soil pH are not altered and the dissolved organic matter (DOM), known to influence Cd availability, is not diluted. As such, the true in situ Cd concentration can be predicted. The isolation of pore water is usually obtained by centrifugation or by using Rhizon samplers. In total, four studies were found to comply with our criteria, resulting in a total of 151 observations. An overview of $\mathrm{K_D}$ models is presented in Table 4.

To select the best $\mathrm{K_D}$ model, we have evaluated proposed $\mathrm{K_D}$ models against the total data set ($n = 151$). For this, we analysed the logarithmic relationship between the predicted pore water concentrations ($=[\mathrm{Cd}]_{\mathrm{soil}} / \mathrm{K_D}$) by each $\mathrm{K_D}$ model and the measured pore water concentrations ($[\mathrm{Cd}]_{\mathrm{solution}}$). The strongest relationship was found in model 5 ($R^2 = 0.81$), followed by model 2 ($R^2 = 0.80$) and model 4 ($R^2 = 0.80$). Model 5, a model developed using all available observations, was selected for further calculations. Fig. 2 shows the good fit between measured and predicted soil Cd using model 5 when restricting the analysis to soils with total Cd < 1 mg Cd kg^{-1}, i.e. the soil most representative for agricultural soils. This graph also demonstrates that the used

Table 4
Selected regression models for $\mathrm{K_D}$ derived from pore water-based $\mathrm{K_D}$ measurements. The number of observations used to derive the empirical model (n) and the R^2 value for the linear relationship log ($\mathrm{K_D}$ measured) and log ($\mathrm{K_D}$ predicted by the model).

Model	Log $\mathrm{K_D}$ = a + b pH + c log (% OC)			n	R^2	Based on data from
	a	b	c			
1	−1.14	0.56	0.88	56	0.67	Degryse et al. (2003)
2	−0.55	0.43	0.70	47	0.75	de Groot et al. (1998)
3	−2.35	0.78	0.43	31	0.81	McGrath (personal communication)
4	−0.74	0.44	0.90	17	0.79	Nolan et al. (2005)
5	−0.94	0.51	0.79	151	0.71	All data compiled

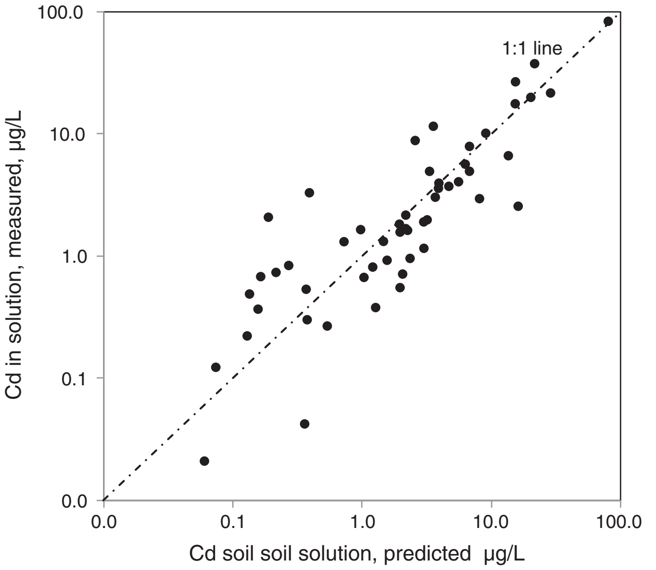

Fig. 2. Predicted (using model 5) and observed soil solution Cd concentration for all soils (pH 3.0–8.6) with total Cd < 1 mg Cd kg^{-1}.
Data from Degryse et al. (2003), de Groot et al. (1998), McGrath (personal communication) and Nolan et al. (2005).

K_D model does not overestimate the dissolved Cd concentration and thus not overestimate leaching.

In 2012, soil pH (0.01 M $CaCl_2$) and organic C content (% OC) were measured over 2000 soil samples from arable land (NGU, 2012). The average soil pH_{CaCl2} of arable soils in Europe is 5.8 (with standard deviation 1.1) and arable soils contain on average 2.5% OC (standard deviation is 1.93% OC). The average leaching is 2.56 g Cd ha^{-1} yr^{-1} when the drainage rate is 0.2 m yr^{-1}. As will be discussed in detail below, this estimate is extremely sensitive to soil pH and to a lesser extent to OC content, which results in a statistical uncertainty of the predicted K_D value. Several studies use a constant leaching flux, e.g. Sternbeck et al. (2011) and Jeng and Singh (1995), fixed at 0.4 g Cd ha^{-1} yr^{-1} for Swedish soils. Moolenaar and Lexmond (1998) derived adsorption models for Cd in the lab, but emphasized that the laboratory situation does not exactly reflect the field situation. They used a leaching loss flux of 1.6 g Cd ha^{-1} yr^{-1}.

3. Model application

The mass balance model (Eq. (1)) was used to predict future Cd concentrations in soils used for arable production (cereals and potatoes). The mass balance used is dynamic, i.e. the output by leaching or crop offtake changes with changing total soil Cd concentrations (de Meeûs et al., 2002). Inputs of Cd are assumed constant over the next 100 years.

The long-term change in soil Cd was calculated from the initial soil Cd concentration ($[Cd]_{soil,\ 0}$) and the soil Cd concentration after 100-year application of fertilizers ($[Cd]_{soil,\ 100}$) as:

$$\%\text{change} = \frac{[Cd]_{soil,0} - [Cd]_{soil,100}}{[Cd]_{soil,0}} \times 100. \qquad (6)$$

This mass balance is made for the conditions representative for the average in EU27 + 1. Next to the estimation of the EU average, a full factorial analysis was used. The model parameters used to obtain the different scenarios under cereal and potato cropping systems are shown in Table 5. Modelling of the future long-term changes in soil Cd concentrations in agricultural top soils predicts soil Cd concentrations to decrease by 15% over the next 100 years in an average scenario, the P10 and P90 range of scenarios are a 64% decrease and a 12% increase (Fig. 3). The scenario's are highly affected by soil pH and, at the average EU soil pH (in $CaCl_2$), most scenarios (up to P75 of scenarios) are negative.

Table 5
Model parameters used for the full factorial analysis to predict the long-term changes of soil Cd in 540 scenarios.

Model parameters	
Atmospheric deposition	0; 0.35, 0.7 g Cd ha^{-1} yr^{-1}
P application rate, yield and TF	Cereal (monocrop): P-rate = 21 kg P_2O_5 ha^{-1}; Yield = 5.1 tonne ha^{-1}; TF = 0.14 Cereal – potato rotation: P-rate = 29 kg P_2O_5 ha^{-1}; Yield = 12.1 tonne ha^{-1}; TF = 0.11 Potato (monocrop): P-rate = 45 kg P_2O_5 ha^{-1}; Yield = 25.9 tonne ha^{-1}; TF = 0.06
% OC	2; 2.5; 3; 4% OC
Soil pH	4.5; 5.5; 5.8; 6.5; 7.5
Cd content of P fertilizer used	36 mg Cd (kg P_2O_5)$^{-1}$
Precipitation excess	0.1; 0.2; 0.3 m yr^{-1}

Next to the European average, the future soil Cd concentration was also predicted for a selection of Member States under cereal cropping systems (Table 6).

In the five regional scenarios, four scenarios have predicted decreases in soil Cd, whereas the scenario for Spain predicts an increase in soil Cd (+15%) (Table 6). This increase is a direct consequence of (i) slow leaching (low precipitation excess), (ii) high soil pH and (iii) relatively high P application rates, when compared to average cereal yields. The 5 regional scenarios reflect regional variability in the Cd mass balance but not parameter uncertainty. Sensitivity analyses are presented to illustrate the most important uncertainties.

3.1. Sensitivity analysis

It is well established that crop offtake strongly depends on the crop type and the soil Cd concentration. Decreasing soil pH enhances crop uptake of Cd. Field data on Cd uptake by numerous plants show that the net effect of increasing soil pH on increasing bioavailability is, on average, only a factor 1.2 per unit pH decrease for maize and potato (McLaughlin et al., 2011; Smolders et al., 2007). This change in TF has only a marginal effect on the Cd balance since crop offtake is small fraction in the Cd mass balance. For example, at the European average, crop offtake is 10-fold smaller than the leaching losses (Table 6).

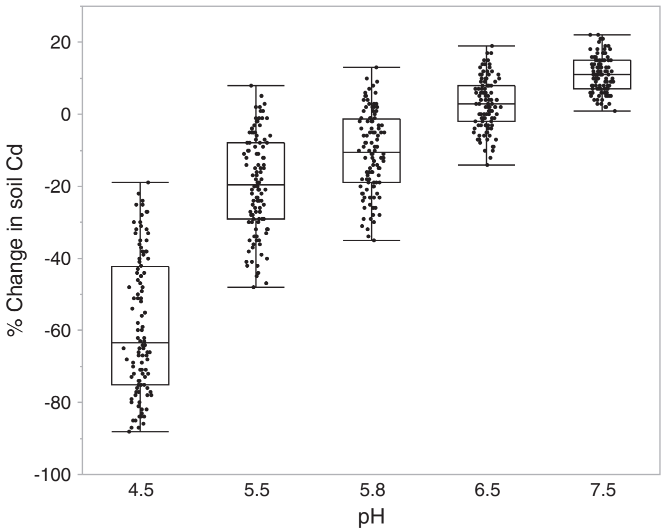

Fig. 3. The predicted % change (min–max and interquartiles; outliers indicated) in soil Cd after 100 years in arable soils for 540 different potential scenarios (Table 5) The median % change is −6%(i.e. decrease), the mean is −15%.

Table 6
Long-term change in soil Cd concentrations after 100-year application of P fertilizers for a set of European countries, with cereals used as reference crop.

Country	Soil properties			Leaching	Atm. Dep.[c]	P fertilizers		Crop yield[f]	Manure[g]	Sludge[h]	Lime[i]	Change in soil Cd	$[Cd]_{soil,\ 100}$
	pH[a]	OC[a]	$[Cd]_{soil,\ 0}$[b]	excess		Application rate[d]	Cd content[e]						
		%	mg Cd kg^{-1}	m yr^{-1}	g Cd ha^{-1}	kg P_2O ha^{-1}	mg Cd $(kg\ P_2O_5)^{-1}$	t ha^{-1}	g Cd ha^{-1}	g Cd ha^{-1}	g Cd ha^{-1}	%	mg Cd kg^{-1}
SE[j]	5.8	4.1	0.25	0.20	0.35	11	4.5	4.7	0.01	0.02	0.04	−15	0.22
DE	6.1	1.7	0.34	0.20	0.25	19	38.9	6.4	0.01	0.05	0.07	−18	0.28
ES	6.4	1.7	0.26	0.05	0.30	28	40.6	3.5	0.01	0.17	0.09	+15	0.30
UK[k]	6.6	2.8	0.30	0.20	0.35	30	22.2	7.0	0.01	0.14	0.14	0	0.30
CZ	5.9	1.9	0.24	0.20	0.40	14	na.	5.6	0.01	0.06	0.09	−12	0.21
EU average	5.8	2.5	0.28	0.20	0.35	21	36.0	5.1	0.01	0.05	0.09	−15	0.24

The parameters used for mass balance calculations for each country are given.
na. Not available.

[a] Soil pH ($CaCl_2$) and OC from agricultural soils were obtained from the GEMAS study (NGU, 2012) unless indicated otherwise.
[b] Initial soil Cd concentration was available from FOREGS and the European risk assessment report (EU, 2007).
[c] Atmospheric deposition (Atm. Dep.) calculated from measurements at EMEP monitoring sites (2012).
[d] P fertilizer application rates for 2010 are available from Fertilizers Europe (2011).
[e] Cd concentration of P fertilizers were obtained from Nziguheba and Smolders (2008), when unavailable the European average as assumed (36 mg Cd $(kg\ P_2O_5)^{-1}$).
[f] Crop offtake was based on cereal production only, a constant TF was assumed at 0.14.
[g] Application rates of manure are assumed constant for all countries (i.e. 0.01 g Cd ha^{-1} yr^{-1}), unless total application rates at country-level are available.
[h] Sludge application rates were calculated as in Table 2.
[i] Unless country averages are available, lime application is estimated to result in 0.09 g Cd ha^{-1} yr^{-1}.
[j] Data on soil properties of agricultural soils in Sweden was obtained from Sternbeck et al. (2011).
[k] Data on soil properties of agricultural soils in UK was obtained from Webb et al. (2001), with conversion of pH (H_2O) to pH ($CaCl_2$).

The predicted leaching highly depends on the reliability of the pore water data. A sensitivity analysis was performed to quantify the effect of the statistical uncertainty of the K_D values on the predicted soil Cd mass balance. From the standard error on the model parameters (fitted by the Equation of model 5 in Table 4), we could estimate the standard deviation on the K_D values from our model for different pH and OC combinations. Fig. 4 shows the variation in percentage change in soil Cd if other parameters are kept constant. Although the error (uncertainty) of K_D is relatively small at low pH compared to high pH, these variations in K_D at low pH will have a much more pronounced effect on the Cd mass balance.

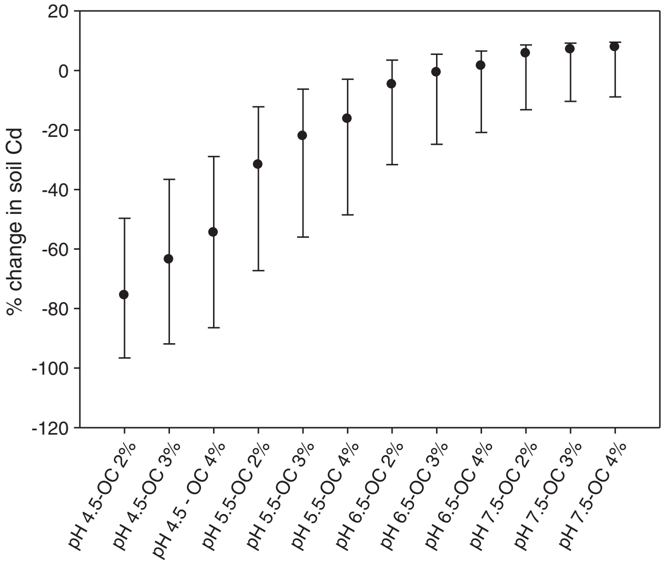

Fig. 4. Uncertainty analysis of the Cd mass balance: effect of uncertainty in K_D values on the % change in soil Cd over 100 years. The error bars represent the 10th and 90th percentile of the predictions based on K_D parameter uncertainty. That uncertainty is based on standard error of parameters of the K_D model (Table 4). Percentage change in soil Cd over 100 years compared to the background Cd concentration (0.3 mg Cd kg^{-1}). For each combination of pH and organic carbon (OC) 1000 simulations were run to cover a full range of K_D values around the mean K_D value. We assumed an atmospheric deposition of 0.35 g Cd ha^{-1} yr^{-1}, a P fertilizer rate of 22 kg P_2O_5 ha^{-1} with 40 mg Cd $(kg\ P_2O_5)^{-1}$, a crop offtake in a cereal monocropping system of 0.21 g Cd ha^{-1} yr^{-1} and a precipitation excess of 0.2 m. The dot represents the predicted flux with mean K_D value.

Leaching is the most important process determining the current mass balance. The predicted annual Cd loss from the plough layer is generally higher than those estimated in most other soil Cd balances (typically < 2 g Cd ha^{-1} yr^{-1}) (Hellstrand and Landner, 1998; Jensen and Bro-Rasmussen, 1992; Moolenaar and Lexmond, 1998; Tjell and Christensen, 1992). In a recent soil Cd mass balance for Australian agricultural soils, predicted leaching of Cd varied from <0.1 g Cd ha^{-1} yr^{-1} in dryland cereal systems to >10 g Cd ha^{-1} yr^{-1} for sugarcane production and annual horticulture, leading to a predicted decline in soil Cd in the future for the latter two scenarios (de Vries and McLaughlin, 2013). That approach used pore water data and excess drainage in the modelled leaching similarly to the approach here. Nicholson et al. (1996) estimated the long-term Cd leaching from the unlimed long-term park grass soils of Rothamsted (UK) using a Cd mass balance. The increase of Cd in the 0–22.5 cm horizon during 1913–1983 was compared with the Cd input by atmospheric deposition (estimated) and by phosphate fertilizers (based on analysis). After accounting for a small (measured) Cd loss by crop offtake, the leaching losses were predicted to range between 0.7 and 3.1 g Cd ha^{-1} yr^{-1} for untreated plots and 2.4 to 4.9 g Cd ha^{-1} yr^{-1} for plots whereto P was applied. The authors estimated a range for the atmospheric Cd input from the average and maximum net annual increase in top soil Cd in 4 different untreated plots of the Rothamsted long-term trials (Jones et al., 1987). Obviously, even the maximum net Cd accumulation in these plots (i.e. 5.4 g Cd ha^{-1} yr^{-1}) is likely lower than the atmospheric Cd input because of Cd losses from these plots. Therefore, the highest estimated Cd leaching from the park grass plots (i.e. 3.1 and 4.9 g Cd ha^{-1} yr^{-1}) may still be conservatively low values. Using our model, we calculated the average annual Cd losses from the P treated plots from the soil properties (soil pH values given in (Nicholson et al., 1994), 0.2 m annual water flux out of the top soil). Our model predicts 4.2 g Cd ha^{-1} yr^{-1} for the P-treated plots. This is within the range of the mass balance estimates of Nicholson et al. (1996).

It is acknowledged that such mass balances do not sensitively prove the Cd leaching. Conceptually, our leaching model assumes that pore water (resident) Cd concentrations denote flux concentrations. Slow desorption of Cd from solid to solution during high flow events may yield lower fluxes of Cd, i.e. flux concentrations may be lower than resident concentrations. However, preferential flow of Cd and colloidal transport may enhance mobility (and result larger losses than predicted) compared to the values predicted from static pore water concentrations. As far as we are aware, only one study has measured

Cd fluxes using wick samplers (flux concentrations) and compared the concentrations with pore water sampled from soil collected near the wick samplers (Degryse and Smolders, 2006). There were three soil profiles at which that was compared and the ratios of Cd concentrations in pore water over those in corresponding leachates (18 months) were 1.4, 0.9 and 1.7, i.e. close to 1.0 corroborating our assumption within that uncertainty. The control site with the lowest soil Cd yielded the largest ratio (1.7). This suggests that our prediction of Cd leaching based on pore water data at low soil Cd may indeed somewhat overestimate Cd leaching.

In another Cd leaching study using 6 different undisturbed pasture soils from New Zealand, it was concluded that the prediction of Cd leaching from pore water composition and rainfall data overestimated Cd leaching by a factor 5, 4 and 2 depending on the soil depth at which the pore water was sampled (Gray et al., 2003). The most relevant depth is the deepest one, corresponding to a factor 2, since the leachate was collected at the bottom of the columns. If correct, the factor 2 has important effects on the estimated EU Cd mass balance. However, the conclusion of that study might be questioned: the soils were undisturbed (unmixed) soil columns, 25 cm high, and Cd concentrations decreased with depth. The pore waters were not collected at the interface where leachates were collected and for which the pore water had to be measured to test the hypothesis whether pore waters denote flux concentrations. In addition, there was no unsaturated water flow since the leachates were collected by gravity, inducing water saturated conditions at the lower interface in which anaerobic conditions develop leading to lower Cd mobility. The higher pH of the leachates than those of the soil is indicative for anaerobic conditions and can reduce local mobility. This suggests that the measured leachate Cd concentrations in that study are lower than values in the field where soils are mainly unsaturated. We have seen such trends before in column studies and concluded that monitoring Cd leaching requires suction to be applied at the bottom of the boundary layer where leachates are collected (Degryse et al., 2007).

A Monte Carlo sensitivity analysis of the projected change in soil Cd was made to identify the variability in Cd trends based on variability of the parameters. This was performed using Risk Solver program for Excel by combining the variability of the atmospheric deposition, P application rate, Cd concentration of P fertilizer, soil pH, OC content and initial soil Cd concentration in Europe and assuming appropriate distributions of the parameters. This analysis entailed 10,000 simulations and again confirmed that soil pH is the most important parameter in predicting long-term change in soil Cd, followed by the initial soil Cd concentration and the OC content of a soil. The Cd concentration of the P fertilizer itself comes only on the fourth position (details of that analysis can be obtained from senior author).

3.2. Comparison with other mass balances

In contrast with other mass balance studies performed in Europe, a net decrease in soil Cd is expected for Europe at the average scenario for cereals (Table 7). In the European Union Cd risk assessment report (EU, 2007), it was calculated that for the European average soil Cd would increase from 0.30 to 0.32 mg Cd (kg soil)$^{-1}$ over 60 years. This difference in result can mainly be attributed to (i) the higher level of P application rate assumed, and (ii) the difference in K_D model used for estimations. In the CSTEE report (2002) soil Cd was estimated to change in 100 years by between −4% and 50% for P fertilizers containing 40 mg Cd (kg P_2O_5)$^{-1}$, which is close to the current European average. Again, different input and output parameters (i.e. atmospheric deposition, leaching, P fertilizer consumption) were assumed (as discussed in detail before). A short overview of similar input and output balances is given in Table 7.

Earlier studies performed by Hutton and Symon (1986) and Nicholson et al. (2003) focussed on making an inventory of Cd inputs to agricultural soils of United Kingdom, whilst in the others output of Cd is also considered. Large differences can be found between previous inventories and more recent estimates (from 2010) for atmospheric deposition, Cd additions by P fertilizers and other diffuse inputs such as manure, lime and sludge. Especially for atmospheric deposition (EMEP/CEIP, 2012a) and P fertilizer use (IFA, 2012), large changes in time have been documented and explain the discrepancy.

There are some data available on recent time trends in Cd concentrations in crops and food. Cadmium concentrations in stored grain samples from a long-term trial in Sweden (60 years: 1918–1980) were measured (Andersson and Bingefors, 1985). An increase was observed up to 1980. Other data from 10 long-term fertilizer trials in Sweden indicate a decreasing trend (about factor 2) in wheat grain between 1980 and 2003 (Kirchmann et al., 2009). The food monitoring programme in Germany noted that wheat grain Cd concentrations decreased from about 0.05 to 0.04 mg Cd kg^{-1} between 1995 and 2005. Such parallel trends in atmospheric deposition (Kirchmann

Table 7
An overview of inputs and outputs (g Cd ha^{-1} yr^{-1}) considered in different European Cd mass balance studies or input inventories.

Reference	Hutton and Symon (1986)	Alloway and Steinnes (1999)	Moolenaar and Lexmond (1998)	Nicholson et al. (2003)	CSTEE (2002)	Sternbeck et al. (2011)	Belon et al. (2012)	Update (2010 as reference)
Country of relevance	UK	Europe	The Netherlands	UK	EU15	Sweden	France	EU27 + 1
Inputs								
Atm. Dep.	3.00	3.00	1.30	1.90	3.00	0.31–0.39	0.25	0.35
P fertilizers	4.40	2.50	1.50–2.50	1.60	0.46–4.14[a]	0.10–0.60[a]	0.98	0.79
Manure and compost	nd.	nd.	0.05	1.4 to 6[b]	nd.	nd.	0.44	0.01
Sewage sludge	0.9	nd.	nd.	0.14	nd.	0.06–0.55[c]	0.08	0.05
Lime	nd.	nd.	nd.	0.14	nd.	0.04	0.04	0.09
Total input	>8.3	>5.5	>2.85–3.85	5.18–9.78	>3.46–7.14	>0.51–1.58	1.79	1.29
Outputs								
Crop offtake	nd.	nd.	0.65[d]	nd.	0.3[e]	0.25–0.84[e]	nd.	0.20[e]
Leaching	nd.	nd.	1.60	nd.	0.31–9.8[f]	0.4[g]	nd.	2.56
Total output	nd.	nd.	2.25	nd.	0.6–10.1	0.65–1.24	nd.	2.76

For this study only the European average was considered.

nd. Not determined or not considered in the study.

[a] Depending on the Cd concentration of the P fertilizer (20, 40 or 60 mg Cd (kg P_2O_5)$^{-1}$) and P fertilizer rate (23 or 69 kg P_2O_5 ha^{-1}) used in calculations.

[b] Depending on the type of manure considered in calculations.

[c] P loads similar to P loads given as mineral fertilizer.

[d] Crop offtake by arable crops only, constant annual crop offtake.

[e] Crop offtake at t = 0 (initial soil Cd concentration is 0.28 mg Cd kg^{-1}), but changes with soil Cd concentration via a transfer function.

[f] Depending on the K_D model (Römkens and Salomons, 1998; McBride et al., 1997) and precipitation excess (0.1 or 0.4 m yr^{-1}) used in calculations.

[g] Leaching is assumed independent of changes in soil Cd concentration, pH and OC.

et al., 2009) may also be affected by recovery from acid rain or declining soil Cd.

3.3. Uncertainties in long-term Cd predictions

The predictions of long-term changes in soil Cd concentrations have relied on the business as usual assumption. This results in an oversimplification of reality as changes can be expected in terms of P fertilizer use, agricultural practices including soil pH control and climate. However, given that no reliable future scenarios can be developed for the all factors; we refrained from making simulations. From the above it is clear than changes in soil pH are likely to have most significant impacts on the balance at current low level input scenarios.

4. Conclusions

The current EU Cd mass balance in a scenario with EU average input/output is negative compared to positive balances for the similar cases that were estimated 10 or more years ago. Soil Cd in cereal and potato cropping systems is predicted to decrease by, on average, 15% over the next 100 years whilst the P10 and P90 range of scenarios are a 64% decrease to a 12% increase. This negative input–output balance was obtained due to the strong reduction of atmospheric Cd deposition data and reduced P fertilizer consumption rates. The predicted regional trends in EU range between 15% increase (e.g. Spain) and 21% decrease (e.g. United Kingdom) and mainly relate to differences in soil pH, precipitation or drainage excess, and fertilizer application rates.

Acknowledgements

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