Abiotic depletion and the potential risk to the supply of cesium

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Abstract

The petroleum exploration industry is the largest end user of cesium where it is employed in oil well drilling fluid. It has recently been broadly reported that the inclusion of cesium into perovskite for photovoltaics and optoelectronics significantly improves their properties. If this element is eventually incorporated into commercial perovskite photovoltaic devices, this usage will add to the amount of Cs required. Herein, mineral resources and the extraction rate of Cs are collected, despite the scarcity and uncertainty of the data. Considering only the Cs resources currently known, as well as assuming the current extraction rate as constant, Cs resources will be completely depleted by 2056. The abiotic depletion potential impact category factor for Cs is calculated to be $1.25 \cdot 10^{-4}$ kg Sb_{eq}. The supply risk of Cs is obtained considering that either a) Canada and Zimbabwe are the main producers or b) China controls all production. The results concur that there is an increase in the supply risk when all Cs production is concentrated in a single place.

Keywords

Cesium, Pollucite, Perovskite, Supply risk, Abiotic depletion potential impact category

1 Introduction

Nowadays, the valuable role of cesium in halide perovskite-based photovoltaics and optoelectronics is growing thanks to the properties obtained when this element is included as the inorganic cation in the halide perovskite. The use of cesium (Cs) confers on perovskite solar cells an increased stability, reproducibility and efficiency, besides decreasing the annealing temperature for the crystallization of perovskite film (Arafat Mahmud et al., 2018; Saliba et al., 2016; Singh and Miyasaka, 2018; Sutton et al., 2016). In fact, Cs is present in most of the solar cells that have achieved high photoconversion efficiency, and also in perovskite LEDs with record external quantum efficiency (Chiba et al., 2018). These attributes have boosted the broad interest in this element among the optoelectronic community.

However, the principal applications of Cs and its compounds are found in petroleum exploration and in the chemical industry. The petroleum exploration industry is the largest end user of Cs in the form of cesium formate. This is used as oil well drilling fluid. The chemical industry exploits the high reactivity of Cs where it is used as a catalyst in various applications. Other specialized applications include, Cs based atomic clocks, global positioning satellites, night vision technology, scintillators and as a propellant agent (Chen et al., 2018; Fortier et al., 2018; Gupta et al., 2009; Hoff et al., 2017; Li et al., 2018; Martínez-Torrents et al., 2018; Shi et al., 2010; Stand et al., 2019). In medicine, Cs isotopes are used to treat cancer (Parashar et al., 2015). Non-radioactive Cs is also used in alternative medicine for cancer treatment , despite its pernicious effects and the lack of scientific evidence for such applications (Aschenbrenner, 2018). Cs-137 isotope is additionally used to reduce the number of pathogens in both sewage sludge and food (Sivinski, 1983).

Cs is mined exclusively from pollucite (Bradley et al., 2017; Cardarelli, 2018). Pollucite occurrences are reported from approximately 140 locations worldwide (Dittrich, 2017), although at present, only two lithium-cesium-tantalum (LCT) pegmatite deposits are known that contain economic quantities of pollucite mineralization. These are the Bikita LCT pegmatite deposit in Zimbabwe and the Tanco LCT pegmatite deposit in Canada (Bradley et al., 2017). However, the Canadian mine suffered significant mining problems (Tetra Tech, 2013a) and eventually collapsed in 2015, and the Zimbabwe mine has extremely fluctuating levels of production and exportation (Cascadero Copper, 2017; Crook, 2018a).

The potential scarcity of Cs may be assessed using two indicators: abiotic potential depletion and supply risk (Cimprich et al., 2019; Schneider et al., 2015; van Oers and Guinée, 2016). One of the impact categories of life cycle assessment (LCA) is the abiotic depletion potential impact category (ADP). ADP is used to measure the decrease in availability of a resource as a consequence of its being used to produce a certain product (Guinée and Heijungs, 1995; van Oers et al., 2002). The first list of ADP factors (ADPF) assumed the extraction rate of cesium to be equal to that of rhenium (Guinée and Heijungs, 1995) and the last to that of rare earth elements (van Oers et al., 2019).

Disruptions to supply may occur due to governmental interventions, market imbalances or physical impediments within the supply chain (Dewulf et al., 2016). Non-fuel minerals, that are at greatest risk of a disruption in supply, and whose supply disruption would have the most consequences, may be considered critical. Previous work in this field has resulted in several methodologies which have produced a variety of lists of critical minerals (Blengini et al., 2017a; Chapman et al., 2014; Ciacci et al., 2016; Erdmann and Graedel, 2011; European Commission, 2017, 2010; Fortier et al., 2018; Glöser et al., 2015; Graedel et al., 2015, 2012; Hayes and McCullough, 2018; Mancini et al., 2016, 2013; McCullough and Nassar, 2017; U.S. National Science and Technology Council, 2016). However, Cs is one of the materials with the least coverage in the criticality assessments (Erdmann and Graedel, 2011). In 2018, Cs was, for the first time ever, included in the draft list as a critical mineral for economic and national security interests by the US government (Fortier et al., 2018). Note that Cs indicators were not available in previous versions drafted by the U.S. National Science and Technology Council (McCullough and Nassar, 2017; U.S. National Science and Technology Council, 2016).

Potential new uses of Cs for solar cells, or any other application, will be feasible if the supply is guaranteed, based on sufficient mineral resources for a given extraction rate and a lack of disruption to supply, measured by the ADP factor (with interest for LCA practitioners) and the supply risk, respectively.

This paper is focused on collecting the available data, despite the enormous uncertainty of the quantity of mineral resources and the extraction rate of Cs (objective 1). With these data, the ADPF and supply risk indicators for Cs (objectives 2 and 3, respectively) will be estimated.

This triple objective defines the structure of the paper. Section 2, Methodology, is divided into three parts: resources, abiotic depletion and supply risk. The following three sections present the results and discussions of each objective. Section 3 is centered on mineral resources, extraction rate and production, Section 4 deals with abiotic depletion and depletion time, whilst Section 5 considers the supply risk. Section 6 discusses the consequences of abiotic depletion and supply risk to possible new applications of Cs, such as in the manufacture of perovskite solar cells. Finally, the last section presents the conclusions.

2 Methodology

2.1 Resources

The terms reserve and resources are interpreted differently by life cycle assessment practitioners and by mining companies and their stakeholders (Drielsma et al., 2016b). In the mining industry, anything that is referred to as a reserve is both feasible and economical to extract in the current or short-term future. In order to avoid confusion, the terminology defined by CRIRSCO (2006) is used in this manuscript:

- The crustal content (CRIRSCO, 2006) or ultimate reserve (Guinée and Heijungs, 1995) is the total amount of an element in the Earth’s crust.

- Extractable global resource (CRIRSCO, 2006) or ultimately extractable reserve (Guinée and Heijungs, 1995) is the amount of crustal content that will ultimately prove extractable by humans.
- Mineral resource (CRIRSCO, 2006) or reserve base (van Oers et al., 2002) is the concentration of solid material in the Earth's crust that has reasonable prospects for eventual economic extraction.
- Mineral reserves (CRIRSCO, 2006) is the economically mineable part of a measured and/or indicated mineral resource.

The studies by Rudnick and Gao (2014, 2003) provide updated figures on continental crustal content. These data can be used to update the ADPF based on ultimate reserves. The content of Cs in oceanic waters is very low compared with continental crustal content, oceanic water contains 0.37 ppb of Cs (Osichkina, 2006), therefore, within the crustal content, only the continental crustal content is considered.

The potential availability of a metal is a dynamic property, changing with geological discoveries, new technologies and new applications. Therefore it is useful to get periodic snapshots in order to evaluate relative, if not absolute, availability. Estimates for mineral resource serve this function (Graedel et al., 2015). For the present study the mineral resource estimates were obtained from different sources in the literature (Baisong, 2014; Butterman et al., 2004; Cabot Corporation, 2016; Dulaney, 2018; Gamvrelis, 1985; Martins et al., 2013; MMCZ, 2016; Norton, 1973; Simpson and Muir, 1974; Teertstra et al., 1993; U.S. Geological Survey, 2017; Zhao et al., 2017).

2.2 Abiotic depletion

In order to obtain the ADPF, equation (1) was used according to the methodology of the Institute of Environmental Sciences (CML) of Leiden University in the Netherlands (Guinée and Heijungs, 1995). This factor is a relative measure, using the depletion of the element antimony as a reference.

$$\mathrm{ADPF_i} = \frac{\mathrm{DR_i}}{(\mathrm{R_i})^2} \times \frac{(\mathrm{R_{ref}})^2}{\mathrm{DR_{ref}}} \quad (1)$$

Where,

$\mathrm{ADPF_i}$	Abiotic depletion potential characterization factor of resource i (generally dimensionless)
$\mathrm{R_i}$	Crustal content of resource i or mineral resource i (kg)
$\mathrm{DR_i}$	Primary annual production rate of resource i (kg/year)
$\mathrm{R_{ref}}$	Crustal content of reference resource or mineral resource of the reference resource, antimony (kg)
$\mathrm{DR_{ref}}$	Primary annual production rate of the reference resource, antimony (kg/year)

The result is highly sensitive to the size of the assumed stock and variability over time. This has led many to debate which denominator (crustal content, mineral resource or mineral reserves) is the most suitable for ADPF (Drielsma et al., 2016b; Schneider et al., 2015; van Oers and Guinée, 2016). Crustal content is a stable comprehensive dataset that can be used to derive a physical estimate of resource depletion for abiotic resources (Drielsma et al., 2016b; van Oers and Guinée, 2016). However, the ILCD handbook (Hauschild et al., 2011), the Product Environment Footprint, and other researchers (Alvarenga et al., 2016) adopt a version of the abiotic depletion potential calculated using the reserve base. The preferred parameter to describe the stock available for human usage would be the extractable global resource (Drielsma et al., 2016a; Schneider et al., 2015), but this is impossible to determine because of our inability to predict what will ultimately be extracted in the future as technology advances and economic and social conditions evolve.

2.3 Supply risk

Three of the most referenced methodologies for supply risk are considered: EU revised methodology (Blengini et al., 2017a, 2017b); Yale Methodology (Graedel et al., 2012) and U.S. National Science and Technology Council (USNSTC) (Hayes and McCullough, 2018; U.S. National Science and Technology Council, 2016).

2.3.1 Supply risk with the EU revised methodology

Supply risk is assumed to be largely influenced by having a concentrated primary supply because the supply may be interrupted. It should be noted that no direct measure of geological availability is included within this methodology due to the timescales considered (Chapman et al., 2014). The risk of inadequate supply of a raw material to meet industry demand is assessed using the indicator supply risk (SR_{EU}).

In the revised methodology, the actual supply to the EU is used in combination with the global suppliers mix (GS) in order to calculate a more representative measure of the risk to the EU. In the case of Cs, Europe depends completely on import and, as far as it is known, no data are available on Cs imported into the EU. Therefore supply risk is based on global production capacities (Blengini et al., 2017a), according to the equation (2):

$$SR_{EU} = (HHI_{WGI-t})_{GS} \cdot \left(1 - (EOL_{RIR})\right) \cdot SI_{SR} \tag{2}$$

In this formula, SR stands for supply risk. HHI is the Herfindahl Hirschman Index used as a proxy for country concentration; WGI is the scaled World Governance Index used as a proxy for country governance; t equals the trade adjustment of WGI, it is a function of the export restrictions (taxes, prohibitions, quotas, licensing, etc.) and mitigated by bilateral agreement with the EU (Blengini et al., 2017b); EOL_{RIR} is the end-of-life recycling input rate (BIO by Deloitte, 2015; Blengini et al., 2017a); and SI_{SR} is the substitution index related to supply risk; HHI_{WGI-t} is obtained as expressed in equation (3) (Blengini et al., 2017a):

$$HHI_{WGI-t} = \sum_j \frac{S_j^2}{10000} \cdot WGI_j \cdot t_j \tag{3}$$

In equation (3), S_j is the concentration of the j producer country expressed as a percentage.

2.3.2 Supply risk with the Yale methodology

The methodology proposed by Graedel et al. (2012) evaluates the supply risk, SR_Y, on the basis of three components: (1) geological, technological, and economic, (2) social and regulatory, and (3) geopolitical. The short-term perspective (5-10 years) is considered here.

The geological, technological, and economic component comprises two equally weighted indicators: the depletion time (DT) that examines the relative abundance of the metal, and the companion metal fraction (CF) that considers the percentage of the metal mined as a companion rather than being mined principally.

Two indicators, the policy potential index (PPI) (Stedman and Green, 2018) and the human development index (HDI) (UNDP, 2018), are employed to quantify the social and regulatory component. Two indicators, one being the political stability and absence of violence/terrorism index of the worldwide governance indicators (WGI_{PV}) (Kaufmann and Kraay, 2018), and the other being the global supply concentration (GSC) implemented with the Herfindahl Hirschman index (HHI) are adapted to form the geopolitical component.

Each composite score is formed by the average of its component scores, and the final supply risk score is calculated by averaging the three composite scores as indicated in equation (4). Unequal weighting is also an option for the individual analyst (Nassar et al., 2012).

$$SR_Y = \frac{\frac{DT + CF}{2} + \frac{PPI + HDI}{2} + \frac{WGI_{PV} + GSC}{2}}{3} \tag{4}$$

Values for each indicator of equation (4) are obtained as indicated by Graedel et al. (2012). Specifically, GSC is obtained with equation (5) and the depletion time with equation (6).

$$GSC = 17.5 \cdot \ln(HHI) - 61.8 \tag{5}$$

$$DT = t_f - t_o \tag{6}$$

$$R_{t_f} = R_{t_o} - \int_{t_o}^{t_f} (DR(t) - w(t) \cdot EOL_{RIR}) \cdot dt$$

In equation (6), R_t is the mineral resource with a long-term outlook or the mineral reserve with a short-term outlook, and w is the output from the use phase.

2.3.3 Supply risk with the methodology USNSTC

Similarly to the EU methodology, the methodology of the USNSTC (2016) uses two factors to assess geopolitical production: the Herfindahl-Hirschman Index and the Worldwide Governance Indicators. In this methodology, these two factors are differently standardized and combined in equation (7) for a specific year to obtain a pre-normalized or “raw” supply risk, SR_{NSTC}.

$$SR_{NSTC} = \sum S_j^2 \cdot \Gamma_j \tag{7}$$

In this equation, S_j is the concentration of the j producer country expressed as a fraction of one and Γ_j is the country’s Composite Governance Index value, based on an aggregation of the six WGIs. The values of each WGI indicator ($WGI_{j,i}$) are first normalized to range from a theoretical low value of 0 for high governance (low risk) to 1 for low governance (high risk) using the equation (8).

$$\Gamma_{j,i} = 1 - \frac{WGI_{j,i} + 3.5}{7} \tag{8}$$

The normalized values for the six WGI indicators are aggregated into a single value for each country based on their geometric mean, equation (9).

$$\Gamma_j = \left(\prod_{I=1}^{6} \Gamma_{j,i} \right)^{\frac{1}{6}} \tag{9}$$

3 Mineral resources, extraction and production

A total of 31 Cs minerals are known and approved by the International Mineralogical Association. However, pollucite is the sole mineral that produces economic quantities of Cs (Dittrich, 2017). Cesium mineral resources as found in the literature are reported in Figure 1 with data expressed as metric tons of Cs (Baisong, 2014; Butterman et al., 2004; Cabot Corporation, 2016; Dulaney, 2018; Gamvrelis, 1985; Martins et al., 2013; MMCZ, 2016; Norton, 1973; Simpson and Muir, 1974; Teertstra et al., 1993; U.S. Geological Survey, 2017; Zhao et al., 2017). Prospect studies are being performed in other locations although the quantification of these resources are not yet published (Avalon, 2018; Simpson and Geo, 2017).

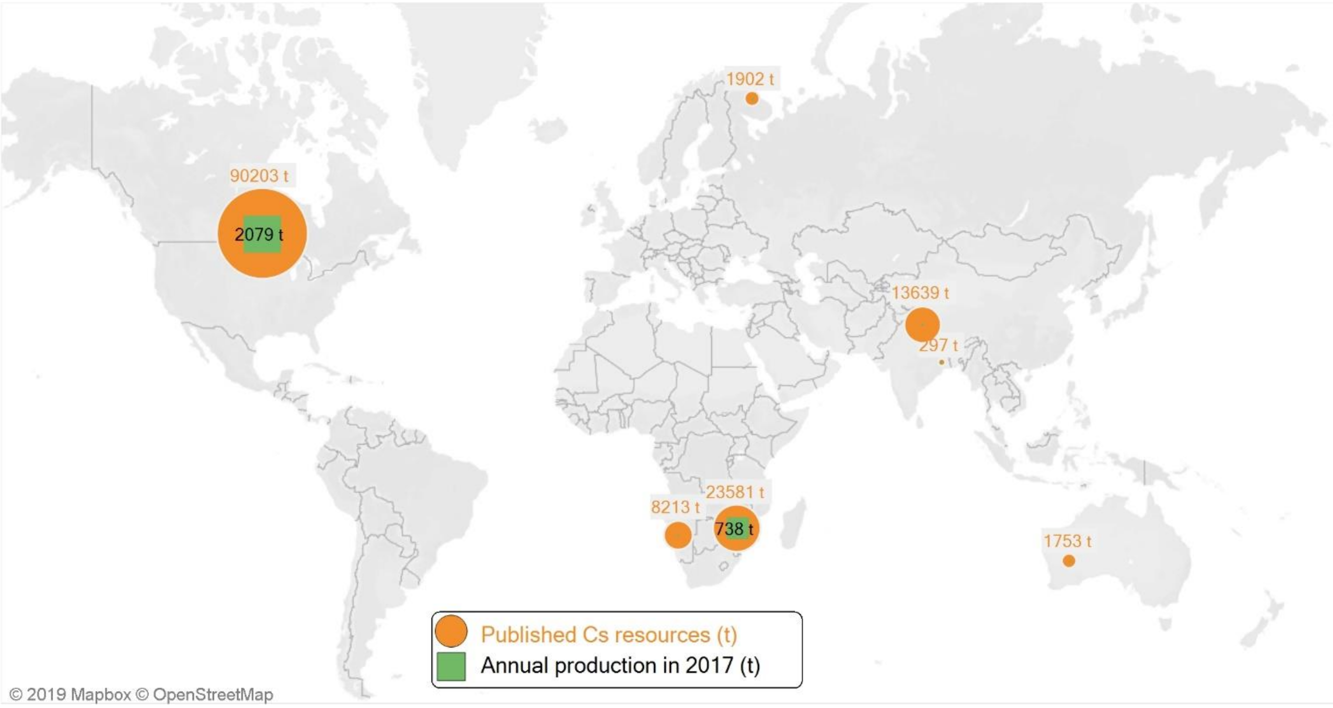

Figure 1. Cs resources and annual production in 2017.

For several decades the global market demand for Cs has been supplied almost exclusively by two companies (Cabot Corporation and Mineral Marketing Corporation of Zimbabwe, MMCZ) operating in two countries (Canada and Zimbabwe, respectively). Other published resources are found in Karibib-Namibia (Gamvrelis, 1985), Tibet-China (Baisong, 2014), Sinclair-Australia (Crook, 2018a), Belamu-India (Som et al., 2007) and Vasin Myl'k-Russia (Pekov and Kononkova, 2010).

The pegmatites at Bernic Lake in Canada (Tanco mine) contain the highest pollucite concentration known to date (Cerny et al., 1998). Cs occurs in three sheet-like bodies (Bannatyne, 1985): the largest one reported reserves (at the end of 1982) of 317,000 tons of pollucite, grading 23.9% Cs_2O, and represents a rather unique economic concentration of pollucite, about 75% pure in the bulk of the zone (Cerny et al., 1998); 54,000 tons of slightly lower grade and 145,000 tons of 5% Cs_2O. The Tanco mine was the world's largest supplier of cesium (Butterman et al., 2004). Tantalum (Ta_2O_5), spodumene (Li_2O), and pollucite are mined concurrently from the same deposit. Between 1969 and 1975, shipments of pollucite (385 t Cs_2O) were made primarily to the U.S.S.R., with other shipments going to Europe, U.S.A. and Japan. Since late 1976, export to communist countries has been prohibited but shipments continue to be made to other countries (Bannatyne, 1985). In 1993, Cabot Corporation acquired Tanco (Tanco Mine, 2009). Up until 1997, all pollucite ore was mined, crushed to order and shipped as raw product. Tanco's annual production was up to 1,000 tons which represented approximately three quarters of the pollucite ore produced worldwide (Cerny et al., 1998). In 1995, Cabot Corporation started Cabot Specialty Fluids and began construction of a pilot plant for the production of Cs-formate, an offshore drilling mud that is used by the petroleum industry. In 1997, the plant was commissioned and Tanco also began mining pollucite ore to supply the plant. The original plant was designed to produce 500 barrels/month of cesium formate. In 1999, expansion of the plant allowed for the production of 700 barrels/month. The first field trial of cesium formate brine was completed in September 1999 by Shell (Tanco Mine, 2009). From 1999 to 2000, the plant was deactivated due to a temporary drop in oil prices. In 2001, the plant underwent a further expansion in order to accommodate the manufacturing of conventional Cs chemicals (Martins et al., 2013).

During its last years, the operation's mining and milling production capacities were 1,000 t/day with typical daily targets of 545 t/day tantalum, 300 t/day spodumene, and 100 t/day pollucite (Tetra Tech, 2013a). Reserves of the plant were of 30000 barrels of cesium formate solution (Downs, 2009). Bernic Lake mine closure was forecast for the year 2018 based on the reserves and mining levels (Tanco Mine, 2009). Nevertheless, extraction rates of pollucite were diminished due to stops caused by significant quantities of rock falling from the ceiling in 2010 and 2013 (Tetra Tech, 2013b), and finally the mine collapsed in 2015. Interestingly, during its last years, Cabot was only mining pollucite (Tetra Tech, 2013b).

The other supplier, the Bikita Mine in Zimbabwe, has extremely fluctuating levels of production and exportation of pollucite for the chemical market. Its estimated annual production rate included in Figure 1 is the average value from years 2013 to 2016 (MMCZ, 2016), although informal sources indicate all the production is from their stock piles (Cascadero Copper, 2017). From 1966 to 1980 the reported extraction of pollucite was 702 t (107.5 t of Cs)

(Gamvrelis, 1985), no data was obtained from 1981 to 2011 and the production from 2013 to 2016 was 3131.5 t of Cs (MMCZ, 2016).

Cesium formate brines are typically rented by oil and gas exploration clients. After completion of the well, the used cesium formate brine is returned and reprocessed for subsequent drilling operations. The formate brines are recycled with an estimated recovery rate of 85%, which can be reprocessed for further use (Cabot Corporation, 2017).

Pollucite is processed into a range of Cs-containing products by other companies such as Cabot (USA), Albermale (Germany) and several Chinese companies (Shangai China Lithium Industrial, Sichuan Brivo Lithium Materials, Nanjing Taiye Chemical Industry, Sinomine Resource, Shanghai Oujin Lithium Industrial, Shangai Energy Lithium Industrial, etc.).

Supply limitations in the future could lead to an increase in price, therefore other companies have found it more attractive to exploit new mines (Avalon, 2018; Cascadero Copper, 2017; IIR, 2018). In the last trimester of 2018 a new pollucite mine was opened in Australia. 7,500 t of mineral will be crushed and shipped to Canada to be converted into cesium formate by Cabot (Crook, 2018b). Monthly shipments are planned until all pollucite has been exported in 2020 (Pioneer Resouces, 2019).

The production of Cs, as reflected in Figure 1 and described above, may change dramatically with the cessation of mining in Canada and Zimbabwe. In addition, during the first trimester of 2019, Cabot Corporation entered into an agreement to sell its Specialty Fluids Division, including the Tanco Mine in Canada (Tullo, 2019), to Sinomine Resource Group Co Ltd., the largest producer and supplier of cesium salt in China (Asian Metal, 2018).

The uncertainty of the supply chain and the change in ownership of the supply during 2019 led us to define two scenarios to estimate the supply risk in Section 5. These two scenarios have been selected based on Cs supply until 2019, called scenario 1, which has signs of exhaustion, as previously mentioned, and the new scenario where all the production is limited to a single country, specifically China, called scenario 2.

4 Abiotic depletion and depletion time

An abiotic depletion factor for Cs based on the crustal content was first obtained by Guinée and Heijungs (1995). Herein, the extraction rate of cesium for 1995 was assumed equal to that of rhenium due to a lack of data in the literature (van Oers et al., 2002). In the review and expansion of the factor using the reserve bases of van Oers (van Oers et al., 2002), the abiotic depletion factors for Cs were stated as not available. More recently, an update for the year 2015 of the abiotic depletion factor for Cs was provided by van Oers et al (2019). However, production rate of Cesium was estimated from the amount of rare earth oxides. New abiotic depletion factors are estimated for the year 2017 (Table 1).

Table 1. ADPF for cesium with extraction rates and reserves from 1995 to 2017. The source is indicated next to each value.

	1995 (Guinée and Heijungs, 1995)	1999 (van Oers et al., 2002)	2015 (van Oers et al., 2019)	2017 Estimated
Primary production rate Sb (ton/year)	$6.06 \cdot 10^4$	$1.22 \cdot 10^5$	$1.42 \cdot 10^5$	$1.5 \cdot 10^5$ (U.S. Geological Survey, 2018)
Sb resource (ton)		$3.20 \cdot 10^6$		$4.30 \cdot 10^6$ (U.S. Geological Survey, 2009)
Crustal content Sb (ppm)	0.2		0.4	0.4 (Rudnick and Gao, 2014)
Primary production rate Cs (ton/year)	29	NA	$5.93 \cdot 10^4$	2,817.1
Cs resource (ton)				96,865
Crustal content Cs (ppm)	1		4.9	4.9 (Rudnick and Gao, 2014)
ADPF resource Cs (kg Sb_{eq})		NA		37
ADPF crust Cs (kg Sb_{eq})	$1.92\ 10^{-5}$	NA	$2.78 \cdot 10^{-3}$	$1.25\ 10^{-4}$

The parameter with the highest change is the production rate of Cs (two orders of magnitude higher). Crustal content of Cs has evolved from 1 ppm to 2 ppm (Rudnick and Gao, 2003) and finally 4.9 ppm (Rudnick and Gao, 2014). Cs is abundant in the crustal content, however the mineral resources are scarce. Therefore it is interesting to observe the ADPFs for both resource and crust. Cs resource is estimated by including reported mineral resources and production extraction. Note in Table 1 that a value of the ADPF mineral resource for cesium higher than 1 indicates a rate of depletion greater than that of antimony (Sb).

The ADPF of Cs based on crustal content indicates a low risk of depletion as a consequence of the above-mentioned abundance in the crust. Compared with the other 118 elements, 38 elements have a higher risk of depletion (van Oers et al., 2019). The result of the ADPF of Cs based on mineral resources is substantially different, indicating a high risk of depletion. Only germanium, gold, indium and thallium have higher factors (van Oers et al., 2002).

Depletion time is estimated over the short-term and long-term with equation (6), using the data pertaining to changes in extraction and production in the last twenty years as presented in Section 3 and using the data from Table 1. The primary production of Cs is considered constant and the secondary resources are estimated to have a lifetime of two years using a spreadsheet from 2001 (Downs, 2009) and a constant recycling input rate of 85% of the fraction used as formate brine sent to re-manufacture, representing 75% of global cesium consumption (Cascadero Copper, 2017). For the purpose of estimating depletion time, the secondary Cs is assumed to be recycled for any future usage. If Cs resources are not increased, either by accounting for as yet unreported resources or by finding new deposits, and assuming as constant the current extraction rate, these resources would be completely depleted in the year 2055, see Figure 2A.

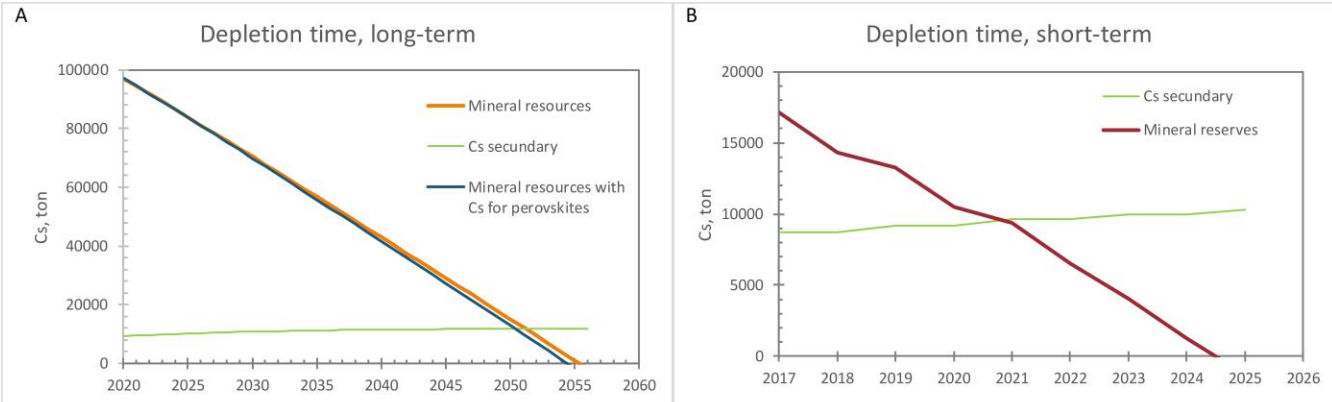

Figure 2. Depletion time. A. For long-term and B. for short-term.

In the short-term, it is assumed that the raw material is obtained from pre-existing stock dating from 2015, that the production of the new Australian mine is added in 2019 and 2020, and from 2021 that all production will be based on secondary cesium. This results in the known mineral reserves being depleted in the year 2025, Figure 2B.

In this calculation, reduction in the use of Cs in the petroleum exploration industry as a consequence of a decrease in oil production due to the increased usage of other energy sources has not been considered.

LCA practitioners usually apply characterization factors from life cycle impact assessment methods, such as ADPF, which are currently provided without uncertainty ranges, although some efforts to reduce this omission are appearing (Igos et al., 2019). In the case of the ADPF for Cs, to the unquantified production rate and to the amount of reserves of Cs are added the uncertainties of the reference mineral, Sb (Guinée and Heijungs, 1995).

Despite these problems in quantifying uncertainty, using the Cs resources and reserves combined with the production data reported in Section 3, the high value of the ADPF based on mineral resources and the very low depletion time, both in the short and the long term, are highly noteworthy.

5 Supply risk

Supply risk is estimated using the two scenarios defined in Section 3 applying the three methodologies detailed in Section 2.3. The data used to estimate the supply risk with the revised methodology of the EU is in Table 2 for the two scenarios. This table includes the average of the WGI six dimensions for the year 2017 (Kaufmann and Kraay, 2018) in the ranges from -2.5 (weak) to 2.5 (strong). In order to create an indicator that represents perceived risk, these values are scaled to the range 0 to 10 and their order inverted such that a higher score corresponds to poor governance and thus to a higher risk. Trade adjustment, t_j, is based on the export restrictions reported in the OECD Inventory of Restrictions on Trade in Raw Materials for minerals (OECD, 2016). Pollucite exports from Zimbabwe are included in the minerals of the lithium group, which is subject to Zimbabwe's non-automatic export licensing regime as well as tariffs (WTO, 2011). The end-of-life recycling input rate is estimated from the cesium formate brine recycling rate (85%) sent to re-manufacture according to material system analysis (BIO by Deloitte, 2015; Blengini et al., 2017a). Recycling of cesium fine chemicals is not considered. The substitution index for supply risk is estimated as one, which means that no substitute is considered (Blengini et al., 2017a). Rubidium could be a potential substitute for cesium, as both have similar physical properties and atomic radii. However, this mineral is not considered as a valid substitute because it is mined from similar deposits, in relatively smaller quantities, as a byproduct of cesium production in pegmatites and as a byproduct of lithium production (U.S. Geological Survey, 2018).

The threshold of the supply risk for potential criticality is 1 (European Comission, 2017). The value of the SR_{EU} applying equation (2) is 0.53 for the scenario 1 (not critical) and 1.51 for the scenario 2 (potentially critical). This last value is similar to that of the supply risk of cobalt, baryte, gallium, helium, vanadium, etc. The high recycling input rate reduces the supply risk according to this methodology, such that in the hypothetical case that the recycling rate was zero, the supply risk in scenario 2 for cesium would be similar to that of rare earth elements.

Table 2. Supply risk with EU Methodology

Scenario	Country	% Primary supply, S_j	WGI_j (0,10)	t_j	$(HHI_{WGI-t})_j$	Supply risk, SR_{EU}
1	Canada	73.8%	1.65	1	0.898	0.53
	Zimbabwe	26.2%	7.46	1.1	0.564	
2	China	100%	4.16	1	4.16	1.51

The data for the determination of supply risk with the Yale methodology are summarized in Table 3, including original values, transformed and fractional contribution for the indicators policy potential index (PPI) (Stedman and Green, 2018), human development index (HDI) (UNDP, 2018), and political stability and absence of violence/terrorism index of the worldwide governance indicators (WGI PV) (Kaufmann and Kraay, 2018) for the year 2017. Transformed values are obtained from the originals as indicated by Graedel et al. (2012).

Depletion will occur in 2025 and the resulting depletion time is 5 years (see Section 4), transformed to an indicator of 98.8 (Graedel et al., 2012). The amount of cesium mined as a by-product is zero, therefore, the companion fraction (CF) (i.e., amount of material globally mined as a by-product), is also zero. Finally, global supply concentration, GSC, is obtained with equation (5).

Table 3. Supply risk with Yale methodology.

		Canada-Manitoba	Zimbabwe	Scenario 1	China	Scenario 2
Mining production		0.74	0.26	1.00	1.00	1.00
Policy potential index PPI (2017)	Original	78.76	29.54	34.14	37.46	62.54
	Transformed	21.24	70.46		62.54	
	Fraction	15.67	18.47		62.54	
Human development index HDI (2017)	Original	0.926	0.535	82.35	0.752	75.20
	Transformed	92.6	53.5		75.2	
	Fraction	68.33	14.02		75.20	
Political stability and absence of violence/ terrorism index WGI PV (2017)	Original	88.57	18.1	29.90	36.67	63.33
	Transformed	11.43	81.9		63.33	
	Fraction	8.43	21.47		63.33	
Depletion time, DT				98.8		98.8
Companion metal fraction, CF				0		0
Global supply concentration, GSC				91.44		100.00
Supply risk, SR_Y				**56.11**		**66.65**

The two scenarios present values of supply risk, SR_Y, in the central part of the range 0-100. No threshold limit is indicated in this methodology to permit conclusions to be made about the potential supply risk. A significant number of metals and metalloids have a similar range, such as Zn, Ge, Sn, Hg, Ba or Pb (Harper et al., 2015; Panousi et al., 2016).

The data used to estimate the supply risk with the methodology of the USNSTC are in Table 4 for two scenarios. This table includes the geometric mean, Γ, of the WGI six dimensions for the year 2017 (Kaufmann and Kraay, 2018) obtained with equations (8) and (9). The value of the SR_{NSTC} applying equation (7) is 0.19 for scenario 1 and 0.54 for scenario 2. The value for scenario 1 is similar to indium, pig iron, ferrovanadium, chromite, etc. (McCullough and Nassar, 2017; U.S. National Science and Technology Council, 2016). The value for scenario 2 would be one of the highest ever reported.

Table 4. Supply risk based on USNSTC methodology.

Scenario	Country	% Primary supply, S_j	S_j^2	Γ_j	Supply risk, SR_{NSTC}
1	Canada	73.8%	0.544	0.26	0.19
	Zimbabwe	26.2%	0.069	0.67	
2	China	100%	1	0.56	0.54

The three methodologies coincide to indicate an increase in the risk of supply disruption with scenario 2, where all the extraction of pollucite is controlled by China, see Figure 3 for the comparison of the min-max normalized supply risks. The degree of the supply risk differs between the methodologies applied, from very significant for scenario 2 (USNTSC), significant (EU revised methodology), to not significant (Yale methodology). These calculations do not consider the effect of an open commercial conflict that could potentially increase the supply risk.

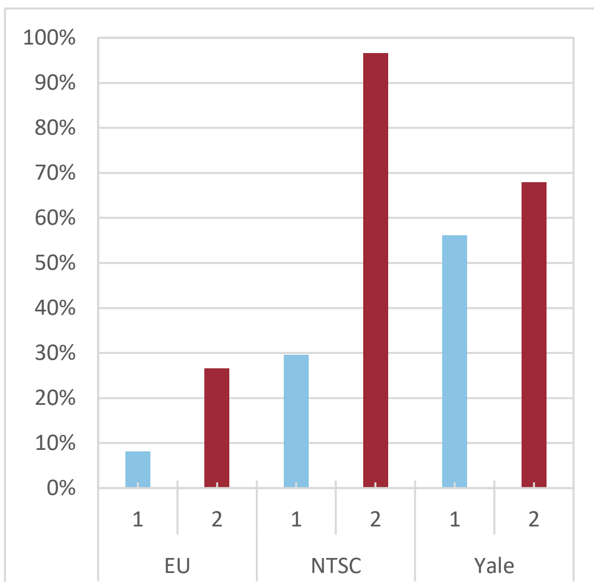

Figure 3. Min-max normalized supply risk for CS with the three methodologies (EU revised, NTSC and Yale) for the Scenario 1 (production in Canada and Zimbabwe) and Scenario 2 (production in China)

Using the Yale methodology generates less difference between the two scenarios compared to the other two methodologies. The explanation is due to variations in the aggregation method (Frenzel et al., 2017) and the choice and weighting of suitable indicators to quantify raw material supply risk (Dewulf et al., 2016; Glöser et al., 2015). The Yale methodology is the only one based on the sum of indicators. The other two methodologies follow a mixed scheme of sums and products. The numerical results of these aggregation methods will clearly differ widely, even if the same indicator values are used. Our results show that the addition of indicators is not sensitive enough. In this paper equally weighting the indicators is used in the Yale Methodology (Nassar et al., 2012), although unequal weighting is also an option to be explored (Nassar et al., 2012).

It is important to note that to be considered critical, in addition to the supply risk other indicators exist such as economic importance according to the EU methodology and production growth and market dynamics, according to the USNSTC methodology.

Parameter uncertainty is attached to all supply disruption probability. The methods require data on raw material production quantities and political stability of producing countries. While the World Bank (Kaufmann and Kraay, 2018) provides confidence intervals for its WGI indicator values, uncertainty information is not typically provided for raw material production data and for the rest of the required parameters for the estimation of the supply risk (Blengini et al., 2017a; Chapman et al., 2014; Glöser et al., 2015; Hallstedt and Isaksson, 2017; Jin et al., 2016). In the particular case of Cs, it is one of the least studied metals and uncertainty about production and reserves are extremely high.

Graedel et al. (2012) described an approach to estimate how the data uncertainty propagates throughout the analysis and how it affects the final results. For all the indicators for which the uncertainty cannot be directly inferred a rubric is utilized to obtain an estimate of the square of the geometric standard deviation and assumes a log normal distribution. By running a Monte Carlo simulation in a software package, the uncertainty of the supply risk is obtained. This approach is used in subsequent assessments using the Yale methodology (Graedel et al., 2015; Harper et al., 2015; Helbig et al., 2016; Nassar et al., 2012; Panousi et al., 2016). Conversely, the EU methodology and the USNSTC lack an approach for uncertainty assessment.

In addition to the data uncertainty, the uncertainty inherent in the supply risk methodology should be highlighted, as shown in Figure 3. The level of supply risk obtained with each of the three methodologies is very diverse, with variable differences when moving from scenario 1 to scenario 2 depending on the aggregation method, as mentioned above. However, in all methodologies the new scenario presents a higher supply risk. Note that supply risk indicators with the EU and NTSC methodology do not take into consideration resource depletion, while the inclusion of the depletion time in the Yale methodology is not sensitive enough. Obviously, resource depletion will affect supply. Future research should address how supply risk needs to include resource depletion factors when resource depletion time and supply risk are on the same time scale.

6 Consequences for new applications: the case of perovskites

The historic climate accord (Paris Agreement, 2015) seeks, at minimum, to limit average global temperature rise to "well below 2 °C" in the present century, compared to pre-industrial levels. The roadmap to 2050 defined by IRENA (2018) considers renewables, in combination with rapidly improving energy efficiency, to form the cornerstone of a viable climate solution. On the basis of their physical properties, meteoric rise in efficiencies, ease of processing, and abundances, perovskites solar cells offer a path to terawatt-scale (TW) energy production (Berry et al., 2017).

The amount of Cs required for photovoltaic panels is very small. For example, assuming a 0.5 micron thick layer of perovskite, with a 10% concentration of cesium (Alberola-Borràs et al., 2018), a solar constant of 1.3611 kW/m^2 (Gueymard, 2018) and an efficiency of 22% (Bella et al., 2018), the required amount of cesium for each square meter of perovskite is only 0.094 g.

Due to an increased capacity of 7 TW from solar photovoltaics, 22% of the world electricity production is estimated to be possible from this source by 2050 (IRENA, 2018). In an extreme scenario in which all seven TWs are obtained using Cs perovskite, $2.34\cdot10^{10}$ m^2 of panels are needed and the extra amount of cesium required would be 2,200 tons from 2025 to 2050.

Theoretically, the supply risk is independent of production. This means, supply risk is not affected by this increase in production. On the other hand, in the aforementioned extreme scenario, the price would probably rise due to the increased pressure of demand on supply and also due to geopolitical tensions caused by the increased economic importance that Cs would have for obtaining energy.

If Cs resources were not increased and assuming an annual linear increase in the extraction rate to cover the new demand for perovskites, the known mineral reserves would be depleted, therefore the production of Cs would need to be from mineral resources that currently are not economically mineable. The resources would be completely depleted one year earlier, see Figure 2. In this calculation, the reduction in the use of Cs in the petroleum exploration industry as a consequence of the decrease in oil production due to the increase of other energy sources has not been considered.

For this scenario, the ADPF based on crustal content remains almost unchanged, from $1.25\ 10^{-4}$ to $1.29\ 10^{-4}$ kg Sb_{eq}. However the ADPF based on mineral resources for the year 2050 will be significantly increased from 37.5 (estimated for the year 2017, Table 1) to $2.86\cdot10^5$ kg Sb_{eq}, the highest value ever reported, exceeding the value of germanium, which is $1.95\cdot10^4$ kg Sb_{eq} (van Oers et al., 2002). This specific case also indicates the high sensitivity of the ADPF, when based on mineral resources, to the potential depletion of said mineral resources.

7 Conclusion

The potential new use of Cs in solar cells, or any other application, will be feasible if the supply is guaranteed with new mineral resources and a lack of supply disruptions. The data on mineral resources and annual production of Cs are very scarce and uncertain; despite the EU and USA being 100%-import-reliant from Canada and Zimbabwe.

However, their stockpiles are likely to be depleting. From the year 2019, Chinese companies controlled the processing of pollucite into a range of cesium-containing products. However, no data about mineral resources or mineral reserves of cesium-containing products are available from this country.

Cs resource is estimated from reported mineral resources and production extraction. If Cs resources are not increased, either by including as yet unaccounted for resources of several countries or by finding new deposits, and assuming as constant the current extraction rate, these resources would be completely depleted in the year 2056, whilst in the short-term, the reserves will be depleted in the year 2025. However, the accuracy of these estimations is somewhat limited by the currently available data.

This is the first time an abiotic depletion factor has been obtained for Cs. The abiotic depletion factor of $1.25 \cdot 10^{-4}$ kg Sb_{eq} has been calculated considering the crustal content of Cs and 37.5 considering the resources of Cs. In previous studies, an abiotic depletion for Cs was not available or it was extrapolated from other elements. The high value of the ADPF based on mineral resources and the very low depletion time, both in the short and the long term, are highly noteworthy.

Two scenarios are considered to calculate supply risk due to the uncertainty of the supply chain and the change in ownership of the supply during 2019: scenario 1 considering the countries Canada and Zimbabwe and production during 2017, and scenario 2 considering 100% of the supply being produced by China.

Supply risk of Cs is calculated by applying three methodologies: EU revised methodology, Yale methodology and that of the U.S. National Science and Technology Council. They coincide in indicating an increase in the supply risk if all the production of pollucite is controlled by a single country. The magnitude of the supply risk for scenario 2 differs between the methodologies from very significant (USNSTC), to significant (EU revised methodology), to not significant (Yale methodology). It is safe to say that the mere addition of indicators is not sensitive enough. These calculations do not consider the effect of an open commercial conflict which would probably increase the supply risk.

There are several further aspects which should be considered in future research work. Regarding the effect of uncertainties, analyses should not only include data uncertainties but also aggregation methods and variations in indicator weightings which can be determined with sensitivity analyses. Future research should address how supply risk needs to include resource depletion factors when resource depletion time and supply risk are on the same time scale.

Any new demand for Cs, for example in the production of photovoltaic energy with perovskites, must take into account the risk of depletion of reserves in the very short-term. The ADPF based on mineral resources is especially sensitive to increases in production rates. This risk could only be mitigated with the exploitation of resources that are currently not economically mineable.

This research draws attention to a concern affecting all current and future Cs consumers. Despite complexity and uncertainty, Cs is a potentially supply risk material and new mineral resources need to be explored and exploited.

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Declaration of Interests

The authors declare no competing interests.

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