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Review

Fluoride network and circular economy as potential model for sustainable development-A review

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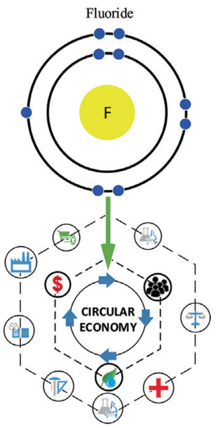
HIGHLIGHTS

- Industrial processes increase fluoride levels and transport in the environment.
- Various fluoride biological pathways increase the risk of toxicity exposure.
- Steering actors must be recognized to attain perpetual sustainable development.
- Circular economy, as a tool to sustainable development, must have same objectives.

GRAPHICAL ABSTRACT



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ABSTRACT

Fluorine is the most reactive elements among the halogen group and commonly and ubiquitously occurs as fluoride in nature. The industrial processes produce fluoride by-products causing the increase of unwanted environmental levels and consequently posing risk on human and environmental health worldwide. This review gives a fundamental understanding of fluoride networks in the industrial processes, in the geological and hydrological transport, and in the biological sphere. Numerous biological pathways of fluoride also increase the risk of exposure. Literature shows that various environmental levels of fluoride due to its chemical characteristics cause bioaccumulation resulting in health deterioration among organisms. These problems are aggravated by emitted fluoride in the air and wastewater streams. Moreover, the current waste disposal dependent on incineration and landfilling superpose to the problem. In our analysis, the fluoride material flow model still follows a linear economy and reuse economy to some extent. This flow model spoils resources with high economic potential and worsens environmental problems. Thus, we intend a shift from the conventional linear economy to a circular economy with the revival of three-dimensional objectives of sustainable development. Linkages between

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key dimensions of the circular economy to stimulate momentum for perpetual sustainable development are proposed to gain economic, environmental and social benefits.

Contents

List of abbreviation

CE	circular economy
CFS	calcium fluoride sludge
EPA	Environmental Protection Agency
FSH	follicle stimulating hormone
GnRH	Gonadotropin-releasing hormone
IQ	intelligent quotient
LE	linear economy
LH	luteinizing hormone
PHS	Public Health Service
SD	sustainable development
TSH	thyroid stimulating hormone
UK	United Kingdom
US	United States
WHO	World Health Organization
WWTP	wastewater treatment plant

1. Introduction

1.1. General background

Fluoride is a persistent and emerging contaminant commonly dispersed in air and further accumulate in the environment. It is considered as the third top air contaminant next to sulfite and ozone (Jha et al., 2008). Many anthropogenic activities (such as mining and product synthesis) can unintentionally concentrate or disperse fluorides in the environment (Piero et al., 2014). It is primarily released as highly phytotoxic fumes from industrial processes such as the coal-fired power plants, aluminum refinery and phosphate fertilizer manufacturing (Koblar et al., 2011).

The immoderate discharge of fluorides into the environment leads to damages to agriculture and livestock (Fuge and Andrews, 1988; MacLean et al., 1968; Ranjan and Ranjan, 2015). Recent developments have also found both bioaccumulation and potential toxicity of fluoride to both plants and animals (Agarwal and Srinivas, 2007; Aguirre-Sierra et al., 2013; Piero et al., 2014). In addition, fluoride bioaccumulation in invertebrates apparently increased with temperature; thus looming problem in global warming can worsen this condition (Del Piero et al., 2012).

A recent laboratory mouse study reiterated the potential fluoride toxicity suggesting chronic exposure and excessive dosage should be avoided (Hellen et al., 2018). Moreover, laboratory-mouse studies were done to simulate potential adverse effects on humans. Reports of massive fluoride exposure have caused severe human fatalities in the past decades (e.g. industrial poisoning in Belgium in 1930 and Pennsylvania in 1948, Hooper Bay outbreak in 1992, and Florida incident in 2015) (Kennedy et al., 2017).

Although fluoride pollution is identified to cause human illness, artificial municipal fluoridation (one of the most controversial and critical fluoride pathways) still persists. Artificial fluoridation has been employed to fight against dental caries in many countries in the past half-century (Worthington et al., 2015). The beneficial aspect of fluoride has been recognized in its uses as an active ingredient in varnish, gel, mouth rinse, and toothpaste over the last three decades (Bansal et al., 2015). Although some health concerns have been voiced, these are considered as unavoidable risks associated with the benefits of fluoride also making fluoridation an ethical issue (Buzalaf, 2018). Furthermore, the added fluoride in supplied municipal water can introduce fluoride in food manufacturing sectors also affecting plants and animals.

In the same way, other fluoride pathways such as low-quality wastewater effluent and uncontained disposed fluoride in landfill become an emerging concern (Ho et al., 2016). The disposal of material resources is a characteristic of the linear economy (LE), terminating in dumping. A shift from LE to a circular economy (CE) is a promising tool of sustainable development (SD) terminating discard through re-utilization and for the protection of the environment. This paper aims to trace the current fluoride networks and to introduce a shift to CE, discussing its potential benefits relative to current fluoride network.

1.2. Physical and chemical properties

Fluorine, with an atomic weight of 19, is the smallest member of the halogen family (1.33 Å in ionic radius). Chemical properties of fluorine are presented in Table 1 (Carter, 1928; Jackson, 2004). Fluorine ranks 13th as the most naturally abundant element, at 0.06–0.09% by weight in the earth's solid crust (Kanduti et al., 2016; Wallis et al., 1996). Being one of the most reactive elements, fluorine does not occur naturally. Fluorine generally forms diatomic gas (F_2) in the environment, having very low boiling point temperature. In addition, fluorine's high energy bonding with electrons forms anionic fluoride (Hamwi, 1996). Fluorides (F^-), typically white or colorless salts, contain the highest electron negativity which makes them distinct from other polyatomic anions and halides (Lucas, 1988). It was also reported that the solubility of fluorine is soluble to inert solvents (Gambaretto et al., 1993). Fluoride can also be highly toxic and become a denaturant of proteins and other vital biological molecules (Mohanta and Jana, 2018).

1.3. Previous fluoride reviews

Illustrated in Fig. 1 is the increase in the number of publications in three different academic search-engines finding (a) “fluoride environmental impacts” and (b) “fluoride toxicity”. This can indicate that there is a growing concern in the impacts of fluoride on the environment and health in less than 20 years. Some review papers discussing fluoride environmental impacts and toxicity are discussed briefly in this section.

1.3.1. Clinical and health reviews on fluoride

After half a century of employing municipal fluoridation, a

Table 1
Chemical properties of Fluorine.

Physical and Chemical Properties	Description
Density	1.7 g/L at standard pressure and Temperature
Oxidation State	−1
Electron Negativity	3.98
Melting Point	−219 °C
Boiling point	−188 °C
Solubility	poorly soluble to soluble
Solubility of Inorganic F^-	0.004–4.054 g/100 cc solution at 25 °C

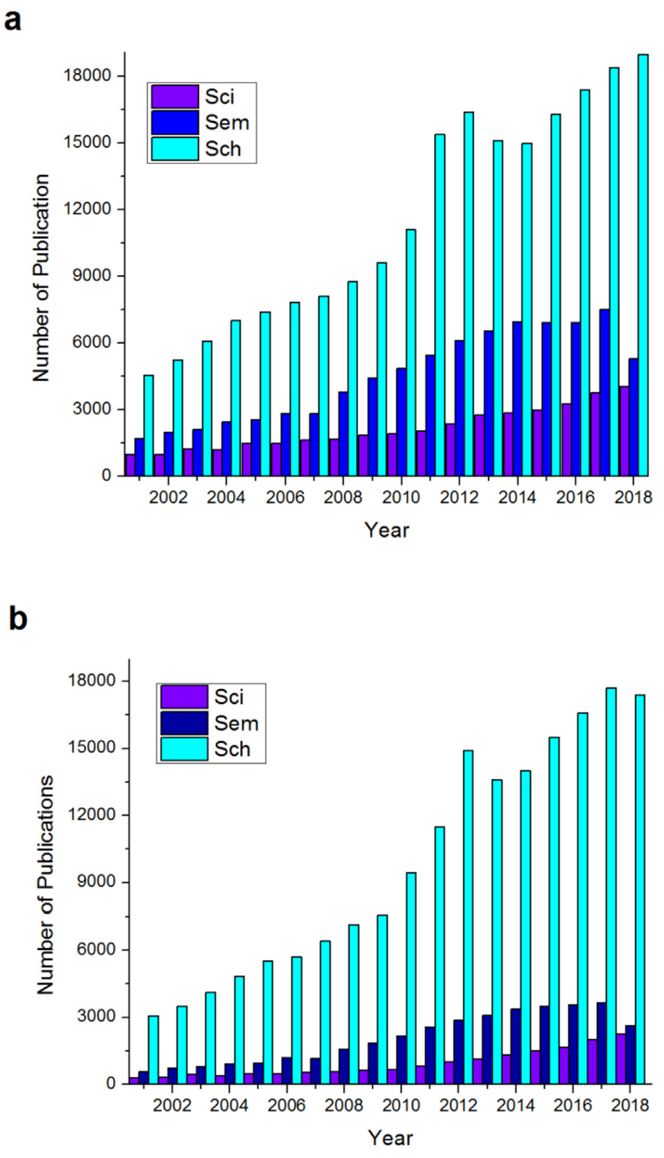

Fig. 1. The Number of Publications from 2001 to 2018 on Fluoride (a) Environmental Impacts and (b) Toxicity taken from different academic search engines Science Direct (🟪), Semantic Scholar (🟦), and Google Scholar (🟦).

systematic review of different researches (known as the York Review) provides an assessment of the evidence of both safety and potential adverse effects of fluoridating the water supply (McDonagh et al., 2000). The authors pointed out that there has been little high-quality data from previous research on fluoride safety and more rigorous research is deemed necessary. Similarly, for the use of fluoride supplements, Ismail and Hassson claim that there are also unsubstantial and incoherent pieces of evidence for primary teeth among children (Ismail and Hasson, 2008). On the other hand, a latter review recommended the used of fluoride supplement to alleviate the high-potential exacerbation of dental caries among children especially for those with fluoride-deficient water supply (Rozier et al., 2010). Recent advancements in the dental fluoride applications highlight the enhancement of fluoride efficacy for preventive dentistry (Bansal et al., 2015).

In 2010, Barbier et al. notably discuss the mechanism of the inorganic fluoride in biological systems and its inherent cytotoxicity (Barbier et al., 2010). The authors further demonstrate the interaction of fluoride in various cytologic processes (i.e. migration, proliferation, respiration, etc.). Correspondingly, a recent review further discussed fluoride toxicity for the general health practitioners providing clinical suitability and safety of fluoride (Kanduti et al., 2016). It emphasizes the dietary sources, metabolism and its effects, and fluoride subsequent toxicity. Another review discussed health problems caused by fluoride but concluded that fluoride is still one of the most beneficial “micronutrients” (Dey and Giri, 2016). Moreover, they reported that chronic exposure to fluoride can adversely affect various organs such as the muscle, kidney, reproductive system, thyroid, nerves, and bones. Both reviews agreed that fluoride can be extremely toxic at high concentrations and fluoride may have various pathways in the human biological circulation. Furthermore, a clinical review highlights the detrimental effects of overdosing fluoride medicaments and misunderstood toxicity (Ullah et al., 2017). The authors further emphasize the fluoride metabolic mechanism together with possible toxicity management.

1.3.2. *Fluoride environmental impacts reviews*

One of the earlier reviews of fluoride in the environment was in United Kingdom providing the local environmental levels in soils, in waters, and in the air (Fuge and Andrews, 1988). Moreover, the authors identified different potential sources of the observed high environmental levels of fluoride.

In North America, a review focused on the possible effects of fluoride-contained effluent from wastewater treatment plant discharged in St. Laurence River (Wallis et al., 1996). The primary purpose of the review was to identify the potential risk of the fluvial biological community and it was concluded that fluoride has no adverse effect on the organisms downstream. In contrast, an earlier review presented various toxicity of fluoride in fishes in laboratory-scale which can be lethal under certain conditions (Sigler and Neuhold, 1972).

Likewise, fluoride toxicity among aquatic organisms has also been reviewed which includes fishes, microphytes, macrophytes and invertebrates (Camargo, 2003). Camargo comprehensively specified both the positive and the negative effects of fluoride. It was also emphasized that environmental conditions highly influence the biological uptake among aquatic organisms.

A comprehensive review further discussed the effects of fluoride in various organisms (i.e. plants, insects, domestic animals and humans) (Zuo et al., 2018). The paper specifically discussed fluoride toxicity in different biological systems causing several pathological aberrations. Furthermore, the review raised that the bioaccumulation among plants can potentially be employed as bioremediation of fluoride contaminated environments.

1.4. *CE and SD*

1.4.1. *Economic models*

SD is basically defined as economic progress without neglecting the environment. SD is typically presented as a meeting point of the three facets: economy, environment, and social justice. Meanwhile, CE is perceived as a tool for SD and described as an emerging concept that is to be fully developed and realized (Suárez-Eiroa et al., 2019). Various literature defined CE as “cleaner production”, “cradle to cradle design”, and “zero-emission” (Korhonen et al., 2018b). The concept of CE is, likewise, intended to uplift a developing economy, maintaining the environment and upholding social justice, by providing an alternative flow model which is both recurring and regenerative in nature unlike the traditional linear flow model (Korhonen et al., 2018b; Millar et al., 2019).

The LE (or linear flow model) is the current practice of the industries following the extraction-production-utilization-disposal flow model. In past decades, it was projected that this economic model is not feasible because of the limited dumping space and finite resources.

Thus, the CE model encourages a departure from the predominant conventional LE because of the apparent dumping of potentially valuable resources. Additionally, there is a consensus that this existing economic flow process undermines these key dimensions of SD (Rees, 2010; Vlek and Steg, 2007).

At present, traditional recycling does not qualify as the CE but simply a reuse economy. The reuse economy anticipates that there are still waste, eventually needing disposal. The reuse economy just delays the process but ultimately result in environmental degradation. On the other hand, the projected full development of CE will ultimately eliminate disposal and will simultaneously generate considerable higher value materials relative to traditional recycling (Ghisellini et al., 2016).

1.4.2. CE and SD (gaps and conflicts)

Recent studies criticize the lack of implementation of CE principles in practice (Flynn and Hacking, 2019; Suárez-Eiroa et al., 2019). Various authors pointed out that there have been some gaps even in the theoretical viewpoint of CE. Critics of CE claimed that although CE is gaining popularity, it is non-univocal in the emerging literature. Kirchherr et al. proved these claims gathering 114 CE definitions through analysis of CE articles (Kirchherr et al., 2017). Moreover, the development of CE models such as “closed-loop” lacks full and analytical understanding of fundamental principles (Korhonen et al., 2018b). The “closed-loop” also confines the CE perspective inside a business model and further prompts just one aspect of SD (the economic aspect).

CE is earlier promoted as an alternative to LE addressing the problems in the three key aspects of SD. However, the recent narratives simply imply that CE is just a model more environment-friendly than the LE but not as the optimum model to attain SD (Millar et al., 2019). In the review of Suarez-Eiroa et al., they revealed that literature recently discussed a single-goal-oriented SD (Suárez-Eiroa et al., 2019). The other issue that superimposed to it, is that the past literature has not distinctly described the relationship and provided an inadequate connection between SD and CE (Kirchherr et al., 2017; Millar et al., 2019).

Kirchherr et al. further revealed that social aspect is the most neglected key aspect and; although earlier authors are more concerned on the environmental goals, most of the literature now emphasized on economic gains (Kirchherr et al., 2017). The initial environmental-focused CE may account for the technological advancement but in a smaller-scale, focusing on how CE may protect the environment. Moreover, the observed current shift to economic gains can be because of the attempt to incorporate this technology into a larger-scale industry.

In addition, the collective perspective is that to achieve SD, it is necessary to balance out (or finding the center) between SD's three key aspects. This further proposes that the three key aspects are apparently “compromising influences” to each other. Much even worse, it can be seen as “conflicting forces” as presented in some studies (Campbell, 2013; Ene et al., 2008; Larson, 2018). Economic progress improves the quality of people's life by providing jobs and market opportunities, enhancing generally the country's development. However, economic progress is stimulated by the production process of different goods and services generating pollution from their waste streams and creates environmental conflicts. Guo and Ma indicated that increased economic development deteriorates the environment and environmental protection can be a very costly objective (Guo and Ma, 2014).

This efficient-seeking character of the economy caused trade-offs not only to the environment but also a threat to social equity. In the past decade, Bardhan warned that some labor sectors (especially agricultural sector) will be left out due to the effects of the economic development and globalization, worsening the poverty (Bardhan, 2001). Moreover, Dastjerdi and Isfahani identified that from the option between the equitable distribution of wealth and economic development, countries typically choose the latter (Dastjerdi and Isfahani, 2011).

Lastly, a call for environmental concern can also cause injustice, an indication of “exclusionary sustainability”. Campbell argued that one-sided environmental concern of the higher classes frequently undermines the interest of the lower classes (particularly the poor and the marginalized) (Campbell, 2013). Thus, the friction caused by compromising and conflicting aspects makes SD an inefficient concept and further expand the gap theory and practice. In addition, a different perspective and new strategies should be developed to reduce these expanding gaps.

1.5. Objectives of this study

During the period of writing to the best of our knowledge, there is no comprehensive review in fluoride pathways forming and presenting the current fluoride network. The reviews in Section 1.3 specifically discussed municipal fluoridation and impacts of fluoride to human health and the environment. These reviews individually deal with the micro-scale development of researches dealing with fluoride while this review aims to fill the gap in different fluoride micro-scale pathways providing a wider perspective. Furthermore, literature typically discusses CE in the context of conceptual material flow and limited in the context of the industrial process. Thus, the focal objective of this review is to map out the flow of fluoride beyond the industrial processes extending to fluoride environmental and biological fate and transport. In the course of the review, we will (1) identify the existing fluoride economy, (2) examine CE principles in the specific material flow (i.e. fluoride) and its almost complete life cycle, and (3) discuss the necessity of transition to CE.

In our review, the industrial sources of fluoride and its possible chemical pathways are highlighted which have not also been included in the discussed reviews in Section 1.3. The fluoride in water, as a regular carrier for environmental transport, will also be discussed with special attention to artificial municipal fluoridation. The last is the impact of fluoride on environmental and human health underlining different fluoride biological pathways reviewing studies after the York review (McDonagh et al., 2000). These three main themes create the picture of the current fluoride network and to have major influences in SD. Despite the existing lapses of CE, the authors recognized the potential of CE to provide a highly-beneficial alternative material flow for fluoride. Thus, the study will specify the necessity of shifting from the current fluoride economy to CE while considering other significant factors and its viability.

2. Fluoride industrial pathway

The role of fluoride within the industrial domain can widely vary from raw material to a reactant or from a product to an unwanted effluent. The first known application of fluoride in soluble form is the NaF-based pesticide since the past century (Metcalf, 1966). In addition to the use of NaF as a pesticide, aerosols containing hydrogen fluoride (HF) are also used for pest-control (MacLean et al., 1968). Hydrogen fluoride, which is further employed for a wide range of materials in the industry, can be produced through the reaction of fluorite and sulfuric acid (eq. (1)).

$$CaF_2 + H_2SO_4 \rightarrow CaSO_4 + 2\ HF \quad (1)$$

The CaF_2 which is also the common form of fluoride extracted from the environment, as a raw material. In 2018, it is estimated that the annual world production and reserves of CaF_2 are 5.8 M metric tons and 310 M metric ton, respectively (USGS, 2019a). The another CaF_2 applications include use of fluorides as flux material for cement calcination (Matsuzawa et al., 2017), additive for improving plastic water resistance (Griffith and Quick, 1970) and resin modifier for hardness and flexural properties (Hammouda and Al-Wakeel, 2011). It is also employed in the application of electric arc furnaces in steelmaking releasing fluoride through the use of fluorite in flux (Alary et al., 1982).

Major industries, however, generate unwanted HF in their processes such as fertilizer, brick aluminum and coal-fired power generating industries leading to environmental pollution. Furthermore, the use of phosphates in the fertilizer industry carries the risk of fluoride contaminants including silicon fluoride and highly corrosive fluorosilicic acid.

2.1. Fertilizer industry

According to US Geological Survey (USGS), the global phosphate industry in 2018 approximately produced about 270 million metric tons (appraised 1.8 B US $) and its use is expected to grow to 51.3 million metric tons by 2022 (USGS, 2019b). The formation of phosphate is formed through the complex reactions in the groundwater.

The increase of CO_2 in groundwater forms carbonic acid, decreasing the pH that drives further reactions of naturally occurring calcium carbonate ($CaCO_3$) and hydrogen phosphate (HPO_4^{2-}). In the presence of fluoride ions, the mineralization of fluorapatite may occur (eq. (2)) which then becomes the main source of phosphorus for fertilizers.

$$5CaCO_3 + 3\ HPO_4^{2-} + F^- = Ca_5F(PO_4)_3 + 3H^+ + 5CO_3^{2-} \quad (2)$$

However, phosphates are the only beneficial to plants and fluorine ions are separated. Phosphoric acid (H_3PO_4) and HF evolves from the decomposition of phosphate in rocks by nitric acid (eq. (3)) or sulfuric acid (eq. 4–5). The retained fluoride in the HNO_3 (eq. (3)) can further react to form NH_4F (Ramteke et al., 2018).

$$Ca_5F(PO_4)_3 + 10\ HNO_3 = 5\ Ca\ (NO_3)_2 + 3H_3PO_4 + HF \quad (3)$$

$$2\ Ca_5F(PO4)_3 + 5H_2SO_4 = 3H_3PO_4 + 5\ CaSO_4 + 2HF \quad (4)$$

$$2\ Ca_5F(PO4)_3 + 7H_2SO_4 = 3H_2(PO_4)_2 + 7\ CaSO_4 + 2HF \quad (5)$$

The H_3PO_4 (in eq. (3)) is separated from $Ca(NO_3)_2$ and further reacted with ammonia (NH_3) to produce ammonium nitrophosphate, a material directly used as fertilizer. Likewise, the produced H_3PO_4 by the wet process (in eq. (4)) will also be reacted to NH_3 to produce ammonium phosphates. In contrast to ammonium phosphates, the single superphosphate fertilizer ($H_2(PO_4)_2$) in eq. (5), is produced in one step from the reaction of sulfuric acid (H_2SO_4) and fluorapatite rocks ($Ca_5F(PO_4)_3$).

The active silica from the phosphate rock can react with HF to produce either silicon tetrafluoride (SiF_4) (eq. (6)) or hydrofluosilicic acid (H_2SiF_6) (eq. (7)).

$$4HF + SiO_2 = SiF_4 + 2H_2O \quad (6)$$

$$6HF + SiO_2 = H_2SiF_6 + 2H_2O \quad (7)$$

Further reactions of byproducts from eq. 6–7 can happen, leading to the generation of H_2SiF_6 and HF.

$$SiF_4 + 3H_2O = H_2SiO_3 + 4\ HF \quad (8)$$

$$SiF_4 + HF = 2H_2SiF_6 \quad (9)$$

The sequence of reactions from eq. 3–9 suggest that most of the fluoride will ultimately form either H_2SiF_6 or HF; these fluorides may enter the acid-digestion liquor as impurities (Wang et al., 2015). The presence of fluorine in the acid digestion liquor causes complications in the separation of solid and liquid components (Abdel-AAL and Amer, 1999; Hussain, 2012). In addition, the free hydrogen fluorides can severely corrode stainless steel pumps, reactors, and stirrers (Kerroum et al., 2018). Essentially, fluorides are unwanted by-products in the fertilizer industry. It is estimated that phosphate rocks may contain 2–4% of fluorine ions (Denizinger et al., 1970). Thus, this unwanted fluoride by-products can reach approximately 5.4–11.8 million metric tons annually.

2.2. Aluminum smelter

The generated aluminum in 2015 is estimated about 58 metric tons (Tressaud, 2019). Cryolite used for the aluminum production may contain 25% fluoride releasing around 19 metric tons of different fluoride compounds in the process (Kvande, 2010). Fluoride pollutants from the aluminum smelter plants have been reported in various studies for the past century (Fuge and Andrews, 1988). It poses serious health risks and environmental damages (Divan Junior et al., 2008; Zhong et al., 2017). Free fluorides can be released by the Hall-Heroult's process with a series of simultaneous reactions (Haupin, 1983).

Molten cryolite (Na_3AlF_6) is the solvent for alumina in the electrolysis process. At very high temperature (1000–2500 °C). Na_3AlF_6 can be dissociated to Na^+ and AlF_6^{3-} (eq. (10)), then, hexafluoroaluminate (AlF_6^{3-}) can further be dissociated to release high reactive F^- (eq. (11)).

$$Na_3AlF_6 = 3Na^+ + AlF_6^{3-} \quad (10)$$

$$AlF_6^{3-} \leftrightharpoons AlF_4^- + 2F^- \quad (11)$$

The dissolution of alumina in molten cryolite and the reaction with AlF_6^{3-} evolves oxyfluoroaluminate ions ($Al_2O_xF_y^{6-2x-y}$) as presented in eq. (12) and 13.

$$4AlF_6^{3-} + Al_2O_3 \rightarrow 3Al_2OF_6^{2-} + 6F^- \quad (12)$$

$$2AlF_6^{3-} + 2Al_2O_3 \rightarrow 3Al_2O_2F_4^{2-} + 4F^- \quad (13)$$

Then, the oxygen contained in oxyfluoroaluminate ions can be discharged when the current is applied through the system and be chemisorbed on the carbon in the anode shown in eq. (14). This would be the source of AlF_6^{3-} for eq. (15)-17. In addition, complex ions can be formed because of oxygen-electrolyte complexation converting AlF_6^{3-} to AlF_4^- shown in eqs. (15) and (16).

$$C + 2\ O^{2-} - 4e^- \rightarrow CO_2 \quad (14)$$

$$Al_2OF_6^{2-} + AlF_6^{3-} + C \rightarrow 4\ AlF_4^- \quad (15)$$

$$Al_2O_2F_4^{2-} + AlF_6^{3-} + C \rightarrow 6\ AlF_4^- \quad (16)$$

The resulting AlF_6^{3-} and AlF_4^- can further be dissociated in a charged Al^{3+} and reactive F^- (eqs. (17) and (18)).

$$AlF_6^{3-} \leftrightharpoons Al^{3+} + 6F^- \tag{17}$$

$$AlF_4^- \leftrightharpoons Al^{3+} + 4F^- \tag{18}$$

Finally, pure and stable aluminum can be produced through the application of current by electrolysis (eqs. (19) and (20))

$$AlF_6^{3-} + 3e^- \rightarrow 3\ Al + 6F^- \tag{19}$$

$$Al^{3+} + 3\ e^- \rightarrow 3\ Al \tag{20}$$

The highly reactive fluoride formed in the Hall-Heroult's process can produce HF from different hydrogen sources such as H_2 in the anode, adsorbed OH, and H_2O in alumina and moisture (Namboothiri et al., 2007). Moreover, HF can also be produced through reactions in eqs. (21) and (22).

$$2\ Na_3AlF_6 + 3H_2 \rightarrow 2Al + 6\ NaF + 6\ HF \tag{21}$$

$$AlF_6 + 3H_2 \rightarrow Al_2O_3 + 6\ HF \tag{22}$$

2.3. Brick kilns

Asia produced 75% of the world's brick which are based in China, Bangladesh and Pakistan (Ahmad et al., 2012). Brick kilns can generate high levels of fluoride (up to 500-10,000 ppm) by heating soils to as high as 900 °C–1500 °C (Jha et al., 2008). There are still fewer studies with regards to the release of fluoride through the brick kilns compared to the aluminum smelters and fertilizer industry. High fluoride level is released through the coal burning and its subsequent transport are emerging concerns to call for more attention (Ahmad et al., 2012; Uooj and Ahmad, 2017). Fluoride generation in the brick kiln will trigger at temperature range 500–600 °C with the proposed reaction in eq. 23–25.

$$OH^- + F^- \rightarrow HF + O^{2-} \tag{23}$$

$$SiO_2 + 4\ HF^- \rightarrow 2H_2O + SiF_4 \tag{24}$$

$$SiO_2 + 4\ F^- \rightarrow 2\ O^{2-} + SiF_4 \tag{25}$$

2.4. Fluoride in coal-fired power plants

Similarly, fluorine in coal is released as fluoride in flue gas by combustion in coal-fired power plants. The utilization of low-quality coals leads to more fluorine impurities to be released into the environment. The sheep's chronic dental fluorosis in Turkey was allegedly caused by the release of fluoride from a coal-fired power plant (Fidanci and Sel, 2001). Under favorable conditions, fluoride can also form hydrofluoric acid which can be corrosive and detrimental to the power plant installations, particularly the stainless steel equipment (Kerroum et al., 2018). It was also reported that fluoride can leach into the coal fly ash that is sequentially dumped in landfills (Piekos et al., 2007). Although, in general, the dumped non-metals have attracted less attention than the dumped heavy metals, non-metals are an important pollutant to be aware of due to the severity that is linked to it. Furthermore, huge amounts of fluoride in landfills may become groundwater contaminants making the groundwater not a readily available water source.

2.5. Other industries

The other sources of fluoride pollutants are steel production, glass making, plastic manufacturing, and glue production. Fluoride emissions from the glass manufacturing were recognized in the past decades with possible chemical reactions shown by eq. 26–28 (Blau and Silverman, 1934).

$$SiO_2 + 2\ CaF_2 = 2\ CaO + SiF_4 \tag{26}$$

$$2\ SiO_2 + 2\ CaF_2 + O_2 = 2\ CaO{\cdot}SiO_2 + 2\ F_2 \tag{27}$$

$$2\ SiO_2 + 4\ NaF + O_2 = 2\ Na_2O{\cdot}SiO_2 + 2\ F_2 \tag{28}$$

Eqs. (29) and (30) describe the formation of toxic hydrogen fluoride compounds in the presence of water.

$$2\ SiO_2 + 2\ CaF_2 + H_2O = 2\ CaO{\cdot}SiO_2 + 2\ HF \tag{29}$$

$$2\ SiO_2 + 4\ NaF + H_2O = 2\ Na_2O{\cdot}SiO_2 + 2\ HF \tag{30}$$

On the other hand, the semiconductor industry utilizes fluoride particularly HF for etching, the chemical stripping of the surface wafer. Kim et al. have traced the HF substance flow revealing that around a quarter of global HF production (about 38,000 tons) utilized in semiconductor industry while 5200 tons HF goes to waste streams, annually (Kim et al., 2017). The most common application is the dissolution of silicon oxide to hydrofluoric acid that forms by-products (i.e. H^+, OH^- and water) that may vary with the prevailing pH in eq. (31) (Kolasinski, 2009).

$$SiO_2 + (n)\ HF = SiF_6 + \text{other byproducts} \tag{31}$$

The waste from semiconductor etching produces large amounts of wastewater with high fluorine content, and its removal also gained interest among researches (De Luna et al., 2009; Huang et al., 2017; Liu and Liu, 2016).

2.6. Immediate post-industrial pathway

2.6.1. Fluoride air pollution

The industries discussed above are the common contributors to fluoride causing air pollution. Fluoride from these industries such as HF, SiF_6, and F_2 are common forms of poisonous gaseous fluoride. Moreover, cryolite, CaF_2, Na, and AlF_6 are forms of particulate fluoride pollutants frequently used in aerosols (Florentina and Io, 2011). The ambient air quality of an unpolluted area is less than $0.1\ \mu g\ F^-/m^3$ but for the areas nearer to fluoride-releasing industries, $2–3\ \mu g\ F^-\ m^{-3}$ are permitted and should not exceed this level (Ranjan and Ranjan, 2015). Industries, such as phosphate fertilizer plants, aluminum smelters, brick kilns, and ceramic factories, are the major source of the gaseous fluoride in the environment, this including the use of fluoride-based pesticide. The uncontrolled HF and SiF_4 gaseous/particulate form from these applications and industries can be an instant air contaminant.

The atmospheric turbulence and wind can transport a large amount of fluoride across significant distances (Dartan et al., 2017). This shows that massive application of fluoride-containing fumes and industrial fluoride effluents might inadvertently affect non-industrial areas. A recent study has shown that fluoride level as high as $9.7\ \mu g\ m^{-3}$ can be observed due to the inter-regional to inter-country fluoride transport (Walna et al., 2013).

At low concentrations, fluoride can already cause leaf burning while the excessive plant uptake can spoil fruits, and deal damage to crops (Ahmad et al., 2012). The topography, the weather patterns and amount of industrial emissions of fluoride are the primary parameters of the fluoride levels in the air (Divan Junior et al., 2008). Although the toxicity due to the possible inhalation of excessive fluoride can be avoided, fluoride deposition in the soil can still lead to other pathways of toxicity.

2.6.2. *Fluoride soil deposition*

The accumulation of fluoride in soil occurs either by the direct deposition of fluoride particulate matter or precipitation of fluoride from the atmosphere to the soil. The movement of the 10-μm-diameter HF-particle is an important field of study as it involves not only an inhalable or respirable particle but also the rate of deposition in the vicinity of the source (Dartan et al., 2017; Zhong et al., 2017). When fertilizers are used, fluoride contaminants left from acid digestion are deposited in soil (Wang et al., 2015). These contaminants originate from phosphate rocks, were 3–75% of fluoride is carried over to the fertilizer (Ramteke et al., 2018). The use of phosphate fertilizer may increase fluoride deposition in soil, leading to fluoride pollution.

Aluminum production is also one of the major contributors to fluoride soil deposition. In 2008, the fluoride levels in the soil in the vicinity of an aluminum smelting plant in Brazil were observed to be distributed disproportionately in a different direction and to decrease exponentially with the distance away from the source (Divan Junior et al., 2008). Furthermore, aluminum fluorides in the form of $AlF_n^{(3-n)+}$ is highly toxic (Frankowski et al., 2010). Many fluoride species, including aluminum hydroxide and oxide and silicate, are resistant to transport and tend to accumulate at the topsoil layer (Luther et al., 1996).

This accumulation results in high fluoride concentration in the soil preventing decomposition of organic substances consequently lowering plant fertility (Zhu et al., 2007). Other factors of fluoride accumulation are fluoride concentration itself, pH, the depth of deposition, the cation exchange, the soil organic matter, and soil classification (Uooj and Ahmad, 2017).

Alternatively, the other pathway of fluoride deposition in the soil is through land spreading. The figures of Eurostat in 2016 show that the most dominant way of disposal of sewage sludge is land spreading applied in agricultural and horticultural purposes (Nakić et al., 2017). This fluoride-contained sewage sludge is produced by municipal wastewater treatment plant which will be further elaborated in Section 3.3.1.

3. Fluoride hydro-environmental pathway

3.1. *Fluoride in natural waters*

In Section 2, anthropogenic activities can exacerbate fluoride accumulation and pollution. However, as salts in rocks, they may be transported through weathering, volcanic eruptions, and geophysical-chemical processes to affect their levels (Banerjee, 2015). Fluoride forms stable hydrogen bonds with water molecules in a solution making fluoride ubiquitously present in most of the natural waters. Moreover, high levels of fluoride can naturally occur in the environment. Thus, the development of cheap and reliable technologies for fluoride detection in waters to avoid its consumption is still gaining interest among researchers (Ebrahim et al., 2019; Kiliçel and Dağ, 2014). In addition, fluoride can be transported and detected in both surface waters and groundwater leading to cross-contamination. Occasionally, very low fluoride levels can also be detected in rainwater. Walna et al. revealed that fluoride levels (>0.1 mg L^{-1}) in rainwater ions due to a suspected transport from a neighboring country is correlated with phosphate, nitrite and the acid-forming ions (Walna et al., 2013). The influence of the water cycle to fluoride fate and transport is illustrated and summarized in Fig. 2 ("The Water Cycle and Climate In California," n.d.).

3.1.1. *Fluoride in confluences of natural water-system*

The interaction between sea, river, and other freshwater-systems can greatly influence transport pollutants including fluoride. Generally, fluoride levels in seawater are relatively high with an average level of 1.3 ppm (ranging from 1.2 to 1.5 ppm) (Ladhar-Chaabouni et al., 2019). On the other hand, fluoride levels are low in natural freshwater systems ranging from 0.01 to 0.03 ppm while those freshwaters with naturally elevated levels of fluoride are

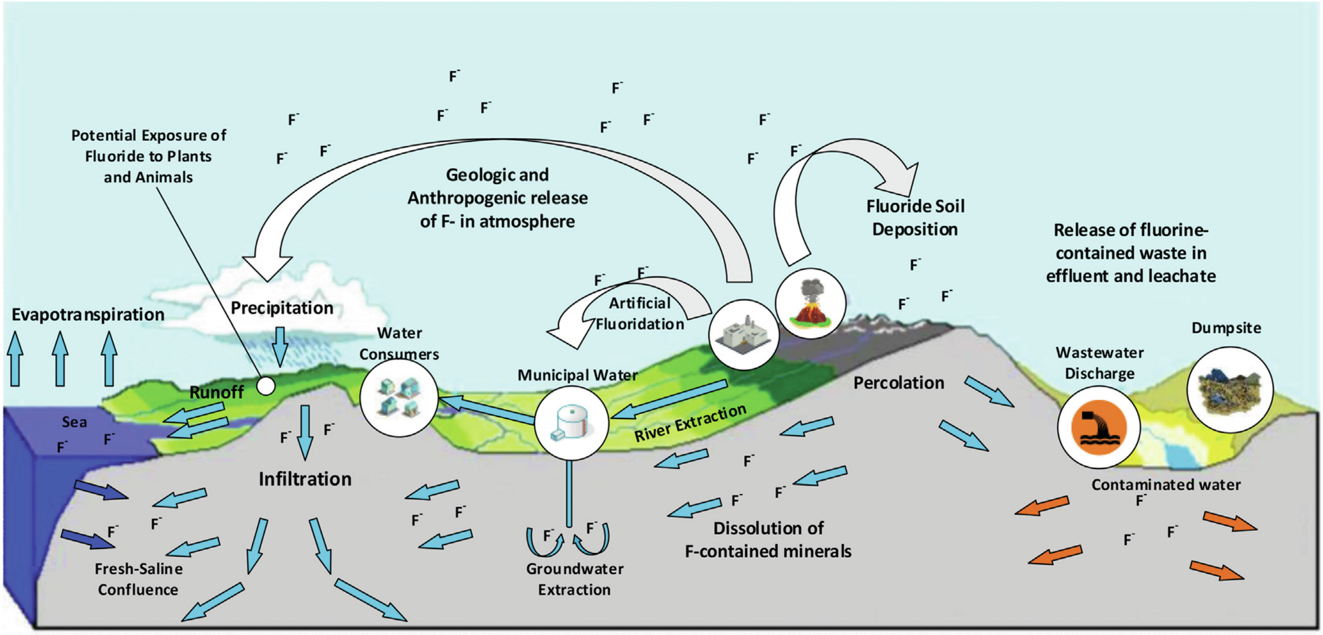

Fig. 2. Hydrologic transport of fluoride in the environment (*adapted from "The Water Cycle and Climate in California"*).

commonly proximate to active geothermal sites (Camargo, 2003).

Recent studies emphasized how the confluence of different water systems affect fluoride levels. El-said et al. primarily indicated that the fluoride level and distribution in Egyptian lagoon can be significantly affected by chlorine levels contributed by coastal water intrusion from El-Maadiya inlet and by surface run-off from agricultural lands (also containing phosphates) (El-Said et al., 2015). The study further revealed that low saturation of sellaïte (MgF_2) and fluorite and relatively high saturation levels of carbonated minerals and fluorapatite can deter fluoride contamination of the lagoon.

In China, Luo et al. likewise presented the relationship between Yun Cheng basin and aquifer contamination (Luo et al., 2018). The authors identified the main source of fluoride contamination are from the use of pesticide and fertilizer, and industrial discharge. Moreover, they further revealed that the interaction between the cation and salts plays a significant role in the increase of fluoride levels in groundwater.

3.2. *Municipal water fluoridation*

As previously discussed, fluoride is traced in water source as a naturally occurring element. In the previous years, there has been deliberately adding fluoride in the municipal water worldwide for fighting dental caries. One of the key uses of fluorides is in water fluoridation, with approximately 17.5 thousand metric tons of fluoride, utilized for this application in 2014 (Connell et al., 2016; US EPA, 2017). Fluoridation is claimed to be safe and still the most effective way of fighting dental decay with 5.49–93.19 US$ benefit cost per capita yearly (Buzalaf, 2018). The study of fluoride for the prevention of dental caries started as an investigation to the discolored or mottled teeth (known as the Colorado brown stain) in the 1900s. Moreover, this mottled tooth was found to be tooth-decay resistant until the investigators figured out that the cause of mottling was the water-borne fluoride. The term tooth mottling, then, became fluorosis.

Fluoridation at 1 ppm F^- has generally utilized and accepted as beneficial to prevent dental caries and lessen fluorosis since half of the 1900s (Buzalaf, 2018; Morés et al., 2011). Moreover, the result of the community fluoridation had satisfying results having a 50% reduction of incidence of tooth decay (Kanduti et al., 2016). Water fluoridation has, then, been considered as a public health measure and as a provider of social justice especially for those who cannot access the proper dental healthcare (Pollick, 2004). On the other hand, the incidence of fluorosis still persisted and considered a necessary risk fighting dental caries; the search for the optimal fluoride intake and concentration, in preventing dental caries and lessening fluorosis with other health effects is still looming concern (Buzalaf, 2018).

Fluoride concentration for the municipal waters may vary from different regulatory bodies or agencies as shown in Table 2. Even US Public Health Service (PHS) suggested range may lead to almost twice the amount of fluoride intake showing significant difference while its contemporary agency US Environmental Protection Agency (EPA) also have different fluoride range. The maximum level of fluoride in drinking water may also differ from country to country given by their respective regulatory bodies.

3.2.1. *Fluoride in groundwater*

Investigations of groundwater, being most employed as a water source and a concern for public health, are more prominent than surface water investigations. The World Health Organization (WHO) estimated average groundwater fluoride level is greater than 1.5 mg L^{-1} (World Health Organization, 2004). The most geogenic occurring fluoride is calcium fluoride (CaF_2 or fluorite) commonly formed as presented in eq. (32).

$$CaCO_3 + 2F^- + H^+ = CaF_2 + HCO_3^- \tag{32}$$

The other common form of fluoride in the environment is fluorite beside fluorapatite (as presented in eq. (2)). It is recently pointed out that the dissolution of these compounds (fluorite and fluorapatite) can be the major cause of groundwater contamination and high fluoride level is estimated to happen in a million year considering water-rock-soil interaction (Banerjee, 2015). In India, fluoride contaminated regions have been investigated and revealed that high fluoride levels in the granitic rocks cause contamination in the region (Shekhar et al., 2017). In addition, the excessive accumulation of fluoride in soil and minerals may lead to unwarranted level in aquifers which can be dangerous to the health of the different organisms exposed to its waters (Zhu et al., 2007). In 2013, it is also pointed out the excessive amount of fluoride (2.22–7.23 ppm) leading to endemic fluorosis, present in the wells in Durango, North Mexico (Molina Frechero et al., 2013).

Furthermore, studies in 2019 also investigated factors influencing fluoride levels in groundwater. In Pakistan, the contaminated groundwater and the influence of unconfined aquifer-surface water systems are explored (Ali et al., 2019). The study shows that pH is primarily responsible in the dissolution of minerals (i.e. calcite, fluorite, halite, and dolomite) significantly affecting fluoride

Table 2
Different limitations of fluoride levels.

Description	Regulatory Bodies/Country	Concentration (ppm)	Reference
Prescribed fluoride concentration from different regulatory bodies for safe consumption	WHO	0.9 to 1.2	WHO (2008)
	US PHS	0.7 to 1.2	Centers for Disease Control and Prevention (2015)
	US EPA	1.4 to 2.4	Hattab (2006)
	US Department of Health and Human Services	0.7	Buzalaf (2018)
	National Health and Medical Research Council (Australia)	0.6–1.1	New South Ministry of Health (2015)
	Fluoridation of Water Supply (Ireland)	0.6–0.8	Beirne and O'Grady (2012)
	Bureau of Indian Standards	1.0	Sharma et al. (2017)
Maximum Levels of Fluoride in drinking water in different countries	United States	4.0	(US EPA, n.d.)
	E.U.	1.5	EU (1998)
	Indonesia	1.5	Ministry of Health of the Republic of Indonesia (2010)
	Philippines	1.0	Department of Health Republic of the Philippines (2007)
	Thailand	1.0	("Notification of the Ministry of Industry No. 332 (BE 2521)," 1978)
	Laos	1.0	(National Environmental Standards No.81 (Laos), 2017)
	Taiwan	0.8	(Taipei Water Department, n.d.)
	Japan	<0.8	Takefuji (2019)

levels. Moreover, the high-evaporation rate being in the arid region can also affect mineral dissolution and the prevailing geochemistry. Alternatively, in Pambar, India, minerals affecting fluoride levels in the groundwater are identified as biotite, fluorite, fluorapatite, and hornblende (Kalpana et al., 2019). Authors further argued that the fluctuations in fluoride levels are affected by the seasonal change. Fluoride levels are decreased in summer due to the groundwater level drop and further deposition of fluoride-contained minerals in the unsaturated aquifer. Furthermore, the deposited minerals are flushed out during the pre-monsoon season increasing fluoride levels. The authors recognized that contamination is due to the variation in groundwater levels, thus, proposing an alternative utilization of the "managed aquifer recharge" (known for groundwater storage for supply) for preventing geogenic fluoride contamination.

3.2.2. *Fluorides in water fluoridation*

NaF, Na_2SiF_6, and H_2SiF_6 are fluoride compounds utilized in the municipal waters. However, these compounds are inherently toxic classified as moderately to gravely hazardous causing eye, skin, and respiratory irritation and its accumulation through ingestion or inhalation further damages various internal organs (Dehesa et al., 1994; Hawley, 1987). In addition, fluorosilicates solutions are very acidic and by-products of the industrial processes (i.e. fertilizer industry) (New South Ministry of Health, 2015). Fluorosilicates also require more delicate handling than NaF but can be more economical for application in larger systems (Pollick, 2004).

The perceived hazardous effect of the fluoride compounds and some ethical consideration are the major reasons for the banning of artificial fluoridation in various countries. Peckham and Awofeso enumerated that there are only eight countries still artificially fluoridating their municipal waters (including US, Australia, Singapore, and Malaysia) (Peckham and Awofeso, 2014). Different investigations suggest that fluoride is not a nutrient and there are lapses in the evidence for the necessity of fluoride intake (Nuffield Council on Bioethics, 2007). Moreover, Peckham and Awofeso sharply argued that fluoride is neither nutrient nor medication and must be identified as a pollutant (Peckham and Awofeso, 2014). Unlike another nutrient, there is no disease such as "fluoride deficiency". Thus, administering fluoride in public water supply triggers ethical issue taking away individual consents (Cheng et al., 2007; Nuffield Council on Bioethics, 2007). Moreover, even it can be considered as medication, fluoride application must depend on the individual's medical requisites (Machoy-Mokrzyńska, 2004).

3.2.3. *Developments in municipal fluoridation*

In the US, artificial fluoridation has been employed in municipal waters since 1945 and reported to be still practiced by about 25 other countries for the prevention of dental caries (Worthington et al., 2015). Since its introduction, municipal water fluoridation has been in constant debates and controversy. After a half-century, the York review has systematically collected and analyzed the studies in the past decades in water fluoridation (McDonagh et al., 2000). It was reported that most investigations in water fluoridation undertaken throughout the world has been in low quality for providing evidence on the efficacy and the understanding of its adverse effects (McDonagh et al., 2000).

It was initially hypothesized that incorporation of fluoride prevented dental caries by reducing the enamel solubility (or the systemic cariostatic effect) (Chan et al., 2004). It would occur by the amalgamation of fluoride to other minerals during enamel development (or the pre-eruptive fluoride application). This mechanism accordingly suggested that there must be fluoride reserves in the body which is the basis for setting the "optimum dosage" for municipal fluoridation.

In contrast, other studies have shown that there is no correlation between the prevention of dental caries and the enamel fluoride levels (Nasir et al., 1985; Retief et al., 1987). Moreover, the reduction of enamel solubility through the incorporation of fluoride was found to have minimal effect in *in vitro* study (Fejerskov et al., 2011). These facts are recently reiterated and further emphasized the topical effect of fluoride (or the post-eruptive fluoride application) supported by both clinical and laboratory investigations (Rošin-Grget, 2013). The topical effect of fluoride was described as the immediate action of fluoride on the surface of the teeth influencing its demineralization and remineralization. Thus, it does not only prevent but may also reverse tooth decay. In this way, it can be deduced that swallowing fluoride in fighting dental caries can be avoidable. Moreover, it is also suggested that the preconception of the "adequate daily intake" is flawed (Peckham and Awofeso, 2014).

3.3. *Fluoride waste disposal*

3.3.1. *Municipal wastewater treatment plants*

The production of the fluoride-containing sludge can be produced in both municipal and industrial wastewater. Although fluoridation of supplied water can contribute to the fluoride levels in the municipal wastewater treatment plant, majority of the fluoride load still comes from used industrial wastewaters (Gehr and Leduc, 2010; Tjandraatmadja et al., 2010). Projection of wastewater discharge is commonly estimated as 75–80% of supplied water suggesting most of the produced water will accrue in wastewater treatment plant (WWTP). This suggests that fluoride levels in WWTP are also dependent on the prevailing fluoride level in the municipal water. On the other hand, the non-accrued water can be accounted as part of run-off and pipe leaks entering environment without prior treatment. Fluoride can further inhibit the nitrification (the main mechanism of biological treatment) while no fluoride removal is reported in the primary treatment (Ochoa-Herrera et al., 2009; Wallis et al., 1996). The primary reason for such occurrence is that the bacteria in the anaerobic digestion is highly sensitive to fluoride leading to a 50% reduction of microbial metabolism (Ochoa-Herrera et al., 2009). Thus, fluoride levels are not only a persistent pollutant in the conventional municipal wastewater treatment plants but can also cause detrimental effect to WWTP efficiency.

3.3.2. *Industrial wastewater treatment plants*

The industrial processes such as described above can most likely generate fluoride in its wastewater effluents. Thus, different wastewater treatment technologies have been developed in recent years to remove fluoride and its possible reuse.

The fertilizer industry utilizes precipitation to remove fluoride in its effluent and to further recover fluoride for other economic benefits. Fluoride can be recovered from H_2SiF_6 solutions in the fertilizer's acid digestion liquor (eq. (7)). The H_2SiF_6 is converted to precipitates through the introduction of sodium (Na) ion (eq. (33)) or potassium (K) ion (eq. (34)):

$$H_2SiF_6 + 2\ NaNO_3 = Na_2SiF_6 + 2\ HNO_3 \tag{33}$$

$$H_2SiF_6 + 2\ KNO_3 = K_2SiF_6 + 2\ HNO_3 \tag{34}$$

The precipitate of the latter is more favorable because of lower solubility and economic value (utilized as an agricultural pesticide, cement binder, and electrolytes) (Wang et al., 2015). In addition, potassium, being essential to crops, will be a supplementary nutrient in the fertilizer. Investigations in improving precipitation in recent years are also reported. The use of ballasting agent in enhancing fluoride removal and flocculation efficiency (Wang et al.,

2013) and the coupled calcium fluoride precipitation with ultrafiltration (Liu and Liu, 2016) have also recently developed.

Alternatively, sorbents are also employed in the fluoride-contained waters. Recently, the use of activated alumina in urban areas is proposed as a sorbent for fluoride removal (Geay et al., 2013). Similarly, it is recommended that lime sludge waste from paper mills can potentially use as sorbent material for fluoride contaminated waters and further produced precipitates of fluorapatite and fluorite (Mohan et al., 2018). However, absorbents and sludge producing water treatment may produce a large amount of waste and still requires landfill disposal.

3.3.3. Fluoride in landfill

Other important sludge disposal method besides land spreading (in Section 2.6.2), is the incineration which sterilizes, significantly reduces weight and volume, and transforms sludge into ash (Nakić et al., 2017). On the other hand, there is substantial leaching of sewage sludge ash which cannot be identified as an inert waste including fluoride (Donatello and Cheeseman, 2013). Similarly, fluoride from coal fly ash in landfills can also leach depending on temperature, pH, and ash/water ratio (Piekos et al., 2007). Moreover, the observed fluoride levels leaching from fly ash can considerably exceed the limit to avoid groundwater contamination.

Thus, the highly soluble fluoride-containing waste can be unfit for direct disposal in a sanitary landfill. The most feasible means to prevent fluoride leaching in landfills are pre-treatment by stabilization and solidification. This pre-treatment of fluoride-containing waste is applied in the pesticide industry (Li et al., 2015). Fluoride contained sludge are also reported to use to stabilize fly ash (Kim and Qureshi, 2006). However, this entails an additional cost for utilizing a considerable quantity of reagents (i.e. lime and cement) and requiring large space upon disposal to landfill.

Thus, redirecting fluoride sludge from landfill disposal to recovery and reuse have been currently emerging. The reuse of the calcium fluoride sludge (CFS) has also attracted concern among researchers worldwide due to severe fluoride pollution potential and rapid depletion of landfill capacity. The feasibility of replacing cement by CFS has also been explored (Lin, 2019). Alternatively, CFS (in the semiconductor industry) is also proposed as a material for manufacturing ceramics (Zhu et al., 2013).

4. Fluoride biological pathway

4.1. Effects of fluoride on terrestrial organisms

Fluoride's small ionic radius causes high biological activity permeating easily to organic tissues (Mondal and Nath, 2015). Although it is perceived to have beneficial effects on humans, there are no apparent benefits to terrestrial plants and animals, especially those sensitive to low fluoride levels. HF, as one of the most phytotoxic air contaminants and released from different industries, pose a serious risk to plants. In previous years, the use of HF pesticide was reported to be persistent in the post-fumigation period leading to chronic exposure and an acute pollutant causing necrosis and chlorosis in plants (MacLean et al., 1968). In a polluted area, plants can absorb an excessive amount of fluoride through its stomata storing it on the tips and edge of the leaf reaching 500–1000 ppm F^- (Florentina and Io, 2011; Ranjan and Ranjan, 2015; Weinstein, 1985).

Similarly, it was reported that the fluoride levels in the soil and atmosphere are correlated to the bioaccumulation of fluoride levels in plants (Stevens et al., 1998; Vike, 1999). This mechanism of bioaccumulation in plants was also proposed as an indicator for both active and passive biomonitoring of airborne fluorides phytotoxic effect (Horntvedt, 1997; Vike, 2005; Yim and Kim, 2016). The fluoride absorption in the plant's stomata affects the photosynthetic process which can sequentially influence the yield and plant growth (Ahmad et al., 2012).

The persistent releases of fluoride by different industries and its accumulation by plants can significantly affect the agricultural sector. Levels of fluoride in corn heads and meadow grass exceeded the feeds maximum allowable content in Slovenia (Koblar et al., 2011). Damages of vegetation due to fluoride have been reported in Taiwan as a result of the ceramic and brick production and in India as a result of the operations of thermal power plants and aluminum smelters (Ahmad et al., 2012).

High levels of fluoride in Turkey is observed near a fertilizer plant and near a coal-fired power plant causing significant decreases in crop yield and severe dental fluorosis to bovine and sheep livestock (Dartan et al., 2017; Fidanci and Sel, 2001). The case of fluorosis is a strong indication of excessive consumption of fluoride which can be through contamination of water or food sources (Brougham et al., 2013). Chronic fluoride toxicity has reportedly been infesting other livestock such as cattle, buffaloes, goats, and camels near these fluoride emitting sources (Ranjan and Ranjan, 2015). Furthermore, other animals with economic benefits are also reported suffering from fluoride poisoning such as large silkworms from mulberry leaves (Zuo et al., 2018). It is suspected that silkworms are grazing mulberry leaves causing reduction of both quality and quantity of the produced silk.

4.2. Effects of fluoride in aquatic organisms

4.2.1. Aquatic animals

Together with the terrestrial organisms, fluoride is also toxic to aquatic organisms through its nature of reducing enzyme activity and disrupting of the metabolic process. In general, fluoride levels and exposure time to fluoride affect toxicity impacts and population growth among aquatic organisms (Camargo, 2003). The exposure time to fluoride, water fluoride levels, and temperature influences significantly fluoride uptake which is more acquirable in water than food intake (Hemens and Warwick, 1972; Nell and Livanos, 1988; Neuhold and Sigler, 1960).

Correspondingly, the prevalent water condition does not only affect biological processes but also the chemical processes in the environment. Tai et al. accounted that the water temperature influences the dissolution of minerals in water (Tai et al., 2006). Hence, it can be deduced that the water temperature might not be the one directly affecting the uptake but rather the dissolution fluoride levels in the water, the primary pathway of fluoride intake. Furthermore, the freshwater invertebrates (e.g. salmon negatively affected by 5.0 ppm F^-) are more vulnerable to fluoride toxicity compared to its marine and estuarine counterparts (Damkaer and Dey, 2011; Hemens and Warwick, 1972; Pankhurst et al., 1980). Camargo inferred that this phenomenon happened because of the higher levels of calcium present in saltwater (Camargo, 2003). As presented in eqs. (2) and (32), calcium carbonate (e.g. calcite and aragonite), can precipitate with fluoride forming fluorapatite and fluorite and further reduce the dissolved fluoride in water, minimizing fluoride exposure and its consequential intake.

Intake and accumulation of different contaminants among organisms are commonly employed as an indicator of water pollution (Larsson et al., 2018; Zanette et al., 2015). Recently, fluoride bioaccumulation in the exoskeleton is utilized as an ecological tracer of origin and transport of organisms. Vighi et al. employed exoskeleton bioaccumulation to investigate krill and fin whale, and fin whale's movement and distribution (Vighi et al., 2015).

Fluoride toxicity and its adverse effects due to the accumulation from the environment has been a vital issue in different studies. Hemens and Warwick revealed that fluoride accumulation of investigated animals (crabs, *Tylodiplax Blephariskios* and shrimps, *Palaemon Pacificus*) due to high levels in the environment suffered from physical degeneration and reproductive aberration (Hemens and Warwick, 1972). Fluoride levels have also been reported to have a sublethal effect (at 5 ppm) and high mortality percentage (at 50–100 ppm) to seawater crustacean (Pankhurst et al., 1980). Likewise, Nell and Livanos earlier investigated the effects of fluoride using spat of oysters (i.e. Sydney rock oysters, (*Saccostrea Commercialis*) and flat oysters (*Ostrea Angasi*)) and have shown fluoride levels inhibit growth by 20% at 30 mg F^- L^{-1} in water (Nell and Livanos, 1988).

The fluoride levels in the environment do not only affect the fluoride intake and health of aquatic organisms but may also significantly influence the food web. Caddisfly larvae, adversely affected by low-level fluoride at 0.5 mg L^{-1}, is a diet among many freshwater fishes (Camargo and La Point, 1995). Although fluoride can indirectly affect the fishes, fluoride can significantly affect these aquatic organisms depending on it as a food source.

Furthermore, krill, one of the most abundant species is also considered to be a major food source for different aquatic animals but also known for its high fluoride content. Moren et al. revealed that Atlantic salmon (*Salmo salar*), Atlantic cod (*Gadus morhua*), rainbow trout (*Onchorhyncus Mykiss*) and Atlantic halibut (*Hippoglossus Hippoglossus*) bioaccumulate more fluoride with the krill and amphipod meal diet than to its fish meal equivalent (Moren et al., 2007). Similarly, traces of fluoride in fin whale is suspected to be due to fluoride bioaccumulation from consumption of krill, its main diet (Vighi et al., 2015). Due to high fluoride content krill has also not been considered as a traditional food source for human. Recently, the organic acid-fluoride extraction from Antartic krill makes it as a potential and alternative food source (Xie et al., 2012).

Different studies also investigated fluoride pathway after aquatic organism intake. Neuhold and Sigler also revealed that active transport of fluoride to the skeletal bones of carp (*Cyprinus carpio*) and the rainbow trout (*Oncorhynchus mykiss*) follow a second-order rate reaction (Neuhold and Sigler, 1960). The observed high-level accumulation of fluoride in the hard tissues is recognized as an organisms defense mechanism against fluoride intoxication inhibiting fluoride circulation within its systems. Correspondingly, fluoride accumulation is also reported in the exoskeleton of marine crustaceans (Sands et al., 1998). In contrast, fluoride is an essential compound strengthening the hard tissue and forming fluorapatite (through the reaction of calcium, fluoride, and phosphorus) in the exoskeleton (Zhang et al., 1993).

Lethal effects of fluoride have also been reported in the different studies in previous decades with indications of fluorosis (Camargo and Tarazona, 1991; Sigler and Neuhold, 1972). Other symptoms are lethargy and anorexia, hyperexcitability (with bradypnea), hyperpigmentation, mucus hypersecretion (coming from respiratory and integumentary organs) and paralysis before eventual death. Recent studies revealed that fluoride exposure activates the fishes biological detoxifying mechanism but can still deteriorate the immune system. In addition, fluoride can cause hypertrophy, melanomacrophage centers buildup (an indication of infection), an aberration of different amino-transferases and headkidney, and headkidney leukocyte apoptosis to African sharptooth catfish (*Clarias gariepinus*) which impair fish over-all health (Singh et al., 2017a). A recent study showed similar symptoms to zebrafish like pro-oxidative stress, pro-apoptotic symptoms, and suppression of pro-inflammatory cytokines expression weakening immunoresistance to pathogenic microorganisms (Singh et al., 2017b). Finally, these reported adverse effects of fluoride to both health and population of the aquatic organism may not only affect the environment but also economic activities particularly aquaculture.

4.2.2. Aquatic plants and microorganism

Unlike aquatic animals, fluoride can have both the positive and negative effects to both macrophytes and microphytes, either inhibiting or improving the population growth which depends on the fluoride levels and exposure, and the species. Likewise, Gao et al. observe simultaneous fluoride effects to *Hydrilla Verticillate* at high concentration (200 mg F^-), reducing carbohydrates, protein, and chlorophyll while stimulating anti-oxidants and plant growth chemicals (Gao et al., 2018). Different studies also investigated the potential use of aquatic plants to bioremediate fluoride providing a strong indication for potential use (Karmakar et al., 2016; Mondal et al., 2014; Sinha et al., 2000). Water lettuce (*Pistia Strationes*), being one of the most studied plants for fluoride phytoremediation in water, is found out as the most feasible candidate for in situ remediation. Karmakar further revealed that bioaccumulation of fluoride by *Pistia stratiotes* follows pseudo-first-order kinetics but can also cause growth reduction (Karmakar et al., 2018).

Reported fluoride resistance of algae widely varies from 25 to 200 mg F^- L^{-1} (Camargo, 2003). McNulty and Lords previously reported that low fluoride concentration could stimulate the metabolism of green alga (*Chlorella Pyrenoidosa*) considerably increasing both the oxygen consumption and the total phosphorylated nucleotides (McNulty and Lords, 1960). Furthermore, some microalgae (such as *Rhodomonas Lens*) may require a certain amount or optimal concentration of fluoride as a growth stimulant (Oliveira et al., 1978). In contrast, exceeding the apparent optimal fluoride concentration might inhibit metabolism and of respective algal species. In 2016, Chae et al. (studying effects of fluoride to freshwater algal species, *Chlamydomonas Reinhardtii and Pseudokirchneriella Subcapitata*) presented that fluoride causes inhibition of growth, organelle potential, photosynthetic ability and cell impermeability consequentially resulting in homeostasis exacerbation (Chae et al., 2016). Unlike plants, we have not seen reports of fluoride phytoremediation using algae. However, there is an apparent growing interest in the bioremediation using fluoride-resistant bacteria (Biswas et al., 2018; Mondal et al., 2015; Saha et al., 2018). To sum up, even there have been a number of investigations done in the effects of fluoride in aquatic organisms, literature is still relatively limited.

4.3. Fluoride fate and adverse impact to human health

Fluoride can be ingested through the consumption of water, food, and medicine with fluoride. In the past decades, the United States Department of Agriculture (USDA) provided fluoride levels in some food groups ranging from 0.01 to 4.0 ppm (USDA, 2005). Bioaccumulation of fluoride from food sources is considered one of the reasons for the increased fluoride level in foods. It is worth noting that tea drinks usually carry the highest fluoride levels at about 3.0 ppm while in some extreme cases can reach as high as 897 ppm F^-. High levels of fluoride in tea drinks can be caused by the easement of fluoride passing through leaves (Fuge and Andrews, 1988; Ranjan and Ranjan, 2015). The other reason might be related to the intake of fluoridated waters and its further application in agriculture and processed products.

Presented in Fig. 3 is the metabolism pathway of fluoride in the human body (Kanduti et al., 2016; Ullah et al., 2017). Approximately ninety percent of fluoride will be absorbed through the gastrointestinal tract commonly influenced by pH, compounds, and fluoride present in the stomach, while the remaining non-absorbed fluoride will be defecated. The absorbed fluoride will enter the bloodstream at 0.01–0.06 ppm (in normal levels). Then, the large amount of it will be excreted as urine through the kidney. The rest of the fluoride will accumulate in the human body both in mineralized tissues (99%) and soft tissues (1%).

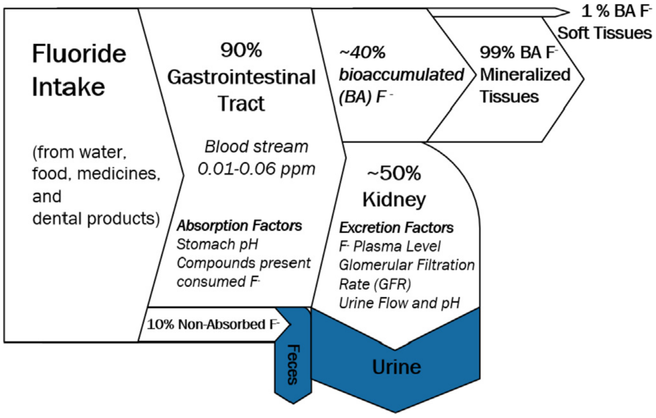

Fig. 3. Fluoride metabolism in human body.

4.3.1. Teeth and bone fluoride toxicity

Less than half of the fluoride intake remains in the body and most of it is deposited on the hard tissues such as teeth, bones, cartilage, and joints. The deposition of fluoride in the hard tissues can be a biomechanism to abate the potential fluoride poisoning because of the affinity of fluoride to calcium dense tissues. Moreover, dental fluorosis is the most commonly reported disease due to the excessive exposure of enamel to fluoride.

Although the dental fluorosis may just look as an aesthetical problem in tooth color, it might also be a possible indication of other more serious diseases related to the endemic skeletal fluorosis. Chronic pain and limited movement of joints and limbs are some clinical complaints related to skeletal fluorosis (Zuo et al., 2018). This can be an early symptom that may lead to the crippling skeletal fluorosis which includes crippled spine deformities (leading to the compression of the spinal cord and further neurological defects) and ligament calcification (Nureddin, 2018).

Skeletal fluorosis can also result in osteosclerosis. Both the osteosclerosis and skeletal fluorosis can be both causes of excessive fluoride intake. One of the first case osteosclerosis due to the intake of fluoridated water (at 12 ppm F^-) was already reported as early as 1943 (Linsman and McMurray, 1943). Osteosclerosis is due to an abnormal hardening of bone because of the increase in bone density. A study further suggested that there was a strong link between skeletal fluorosis and osteosclerosis (when investigating lumbar spine and femur neck bone) estimating one-third of the osteosclerosis incidence in a Turkish city was caused by endemic skeletal fluorosis (Tamer et al., 2007). Moreover, Rajendran revealed in a clinical report (of a 69-year old male patient) that fluorosis caused not only ligament calcification and osteosclerosis in the lumbosacral spine but also osteophytosis (also known as bone spurs) (Rajendran, 2016).

Osteoporosis is another bone disease related to the weakening of the bone which may lead to sequential bone breakage. It was initially believed that the intake of NaF would increase bone mass density as a therapeutic treatment. However, further investigation showed that fluoride conversely increased the risk of bone breakage (Cummings and Eastell, 2018). It was also found that osteophyte which was linked to the endemic fluorosis could worsen the osteoarthritis (Fontes et al., 2001). Furthermore, osteosarcoma is a rare and lethal bone cancer-causing underdevelopment of bones. It is also reported that there is a possibility of a correlation between the fluoride exposure and osteosarcoma which is stronger among males (<20 yrs old) than females (Bassin et al., 2006; Kharb et al., 2012).

4.3.2. Cardiovascular and arterial fluoride toxicity

The heart together with the arteries is a vital organ of uttermost importance in the human body, as a failure of these organs leads to sudden death. Despite this importance, cardiovascular and arterial fluoride toxicity have gained less attention in comparison to the more evident fluoride toxicity on the hard tissues (i.e. the skeletal fluorosis). Blood with nutrients and other important substances for biological processes (transported by circulatory organs) may contain fluoride from inhaled air or metabolized water and food and further, accumulate in these organs. Studies also show that skeletal fluorosis can be an indicator of the potential build-up of fluoride to both the heart and the arteries (Pain, 2016; Panneerselvam et al., 2015). Furthermore, both the clinical and the experimental studies revealed that the increased fluoride exposure induced cardiovascular-related diseases such as periostin deficiency, hyperhomocysteinemia, and hypertension (Oyagbemi et al., 2016; Varol et al., 2010; Varol and Varol, 2012).

Periostin is the protein responsible for the repair of the heart tissues and the growth of the cardiac valves. Thus, periostin deficiency (particularly induced by fluoride) may result in cardiac valve abnormalities and degeneration (Conway and Molkentin, 2008; Varol et al., 2010). Correspondingly, a recent study found specifically that myocardial necrosis can be correlated with fluoride levels in the heart (Li et al., 2012).

Likewise, hyperhomocysteinemia is an aberrant high-level of homocysteine associated with inflammation of the blood vessels and increased the risk of atherosclerosis. Atherosclerosis (a disorder characterized by the massive arterial wall calcification and linked with the risk of atherothrombosis) has also been reported to have a significant positive correlation to fluoride intake (Li et al., 2012). Similar studies correlated enlargement of coronary artery ($\geq$1.5 times of its normal size) and the occurrence of carotid artery atherosclerosis (in China) with the chronic, endemic, and excessive fluoride (Dede et al., 2011; Liu et al., 2014). Liu et al. (2014) further show that the rise in the level of antibody and the reduction of glutathione peroxidase are also correlated. In addition, fluoride intake causes increased levels of calcitonin, a hormone in which elevated levels are linked with hyperhomocysteinemia, coronary vasospasms, ischemia, stroke and heart attack.

High fluoride level can also stimulate generation of haptoglobin, an indicator of a potential coronary vascular disease and hypertension (Susheela and Jethanandani, 1994). Hypertension can subsequently increase the risk of cardiovascular-related diseases. It has also been observed that there were higher rates of abnormal electrocardiograms and hypertension for patients with skeletal fluorosis (Amini et al., 2011; Wei et al., 2013). An experimental study also revealed that NaF can also cause histopathological aberrations to heart (and kidney) inducing hypertension (characterized by increased systolic, diastolic and mean arterial pressure) and cardiovascular complications (Oyagbemi et al., 2016). In addition, oxidative stress, inflammation, and damage in tissues in both heart (and kidney) were also observed.

4.3.3. Fluoride thyrotoxicity

The thyroid is perceived to have the high-absorbing capacity making it prone to fluoride accumulation. However, it is apparently the most fluoride-sensitive among tissues in the body and its follicles can directly be damaged, inducing karyopyknosis (Ge et al., 2005; Selim et al., 2012). Fluoride-anion-contained medicine (i.e. fluorophosphate ($PO_2F_2^-$), fluosulfonate (SO_3F^-), and tetrafluoroborate (BF_4^-)) are branded to have adverse side effects to the thyroid (MZ and Wihardja, 2017). Likewise, increased fluoride levels due to medicaments affect thyroid function by increased calcitonin activity that may manifest with signs and symptoms.

Fluoride, being in the halogen group with iodide (a vital nutrient for thyroid), can also chemically mimic iodide impending its natural transport in the thyroid gland (Selim et al., 2012). Essential thyroid hormones, triiodothyronine (T3) and thyroxine (T4), are composed of iodine atoms. Moreover, various studies attributed the decline of T3 and thyroxine T4 levels and further increase of thyrotropin (or thyroid stimulating hormone, TSH) levels to fluoride exposure causing hypothyroidism (Dey and Giri, 2016; Peckham and Awofeso, 2014; Selim et al., 2012).

Recent studies can still have conflicting claims in the potential correlation of fluoride to the thyroid. In Iran, Ullah et al. claimed that fluoride levels in water even at low concentrations can increase TSH values, despite the integrated program providing supplementary iodine added in salt (Ullah et al., 2017). Moreover, this can be supported by the findings of MZ and Wihardja (2017), reporting fluoride intake (both lower or higher concentration than 1 ppm) generally cause thyroid gland irritation (MZ and Wihardja, 2017). On the other hand, Malin et al. (in Canada) recently asserted that the urinary fluoride levels (an indicator of exposure) do not provide evidence of fluoride influence to thyroid dysfunction, directing the cause of dysfunction to iodine deficiency (Malin et al., 2018).

4.3.4. Fluoride hepatotoxicity and nephrotoxicity

Liver and the kidney are the two organs most vulnerable to fluoride exposure due to fluoride accumulation in the soft tissues. An experimental study revealed that chronic exposure to fluoride can alter both the functional and histopathological characteristics of the liver and kidney (including the heart) (Kumari and Kumar, 2011). Furthermore, a recent study suggested that the changes observed in liver qualities are dependent on both time and fluoride intake (Pereira et al., 2018). Apoptosis of liver sinusoids and of hepatocytes is also reported due to high fluoride dosage (Sahu et al., 2015). High dosages and excessive intake of fluoride can lead to increased levels of fluoride in urine and renal apoptosis through oxidative stress (Yu et al., 2006). Moreover, excessive fluoride intake via water and food is considered as one of the causes of chronic kidney disease in Sri Lanka (Dharmaratne, 2015).

4.3.5. Fluoride neurotoxicity

One of the first laboratory studies comprehensively investigating the fluoride neurotoxicity was the fluoride exposure of rats to NaF in 1995 (Mullenix et al., 1995). The study revealed that the high concentration of fluoride increased the fluoride level in the certain brain regions causing adverse behavioral changes. The applied fluoride concentration in this study is equivalent to the reported human exposure. On the other hand, humans are relatively more sensitive to the effects of fluoride exposure than rats. Thus, more adverse effects are expected to human exposure with the same fluoride level.

Fluoride can specifically permeate to neural tissue and to the blood-brain barrier causing aberration of the brain morphology. Thus, the NaF causing neurodegeneration is identified with the accumulation of fluoride in the brain. Conversely, it does not exclusively happen due to fluoride accumulation in the brain but also due to fluoride accumulation in sciatic nerves and the spinal cord (which must be given equal importance) (Reddy et al., 2011). Moreover, the neurodegeneration observed in this study is characterized by inflammation of mitochondria, hippocampus, and cerebellum, breakage of myelinated fibers, fragmentation of myelin, and vacuolation of Schwann cell in both brain and sciatic nerves. Fluoride could also induce oxidative stresses leading to brain lipid degradation, which is believed to influence mainly the brain pathogenesis (Shivarajashankara et al., 2002). Likewise, chronic fluorosis because of its nature of altering membrane lipids is also described to potentially affect the brain (Guan et al., 1998).

The Harvard Review investigated epidemiological studies relating the endemic fluoride exposures in China to intelligence quotient (IQ) scores for the past 20 years (Choi et al., 2012). This study further reported that children exposed to drinking water with high fluoride levels had 0.45 lower IQ scores relative to those exposed to no or minimal fluoride. Various studies from different regions (China, Mongolia, India, Iran, and Mexico) also reported that the exposure in the endemic fluoride in the drinking water reduce IQ scores and both skeletal fluorosis and urinary fluoride levels could be strong indicators of reduced IQ's (Ding et al., 2011; Lu et al., 2000; Poureslami et al., 2011; Rocha-Amador et al., 2007; Saxena et al., 2012). A threshold fluoride level in drinking water (0.24–2.84 mg L^{-1} with a mean concentration of 1.31 mg L^{-1}) was observed with a 0.59-point reduction in IQ score per 1 mg F^- L^{-1} increase (Ding et al., 2011). Additionally, the exposure to fluoride from the coal-burning was allegedly the cause dental fluorosis which linked to IQ score reduction among children (Li et al., 2009). Recent studies in the US (2015) and in Mexico (2018) also indicated that both pre-natal exposures to fluoride and to fluoridated water are potentially correlated to the incidence of attention deficit hyper-activity disorder (ADHD) among children and adolescents (Bashash et al., 2018; Malin and Till, 2015). These may imply that the neurodegenerative effect of fluoride causes these observed disorders. Recently, Wang et al. proposed a possible mechanism of fluoride-induced neurodegeneration. The authors suggest that important proteins (i.e. cyclic AMP responsive element binding, and brain-derived neurotrophic factor) affecting the neuron developments (crucial for learning and memory) are regulated by the glutathione S-transferase omega-1 expression levels which can be altered by fluoride (Wang et al., 2019).

Moreover, the pineal gland, a small and unique endocrine gland at the brain central region responsible for the circadian rhythm and the production of melatonin, is allegedly affected by fluoride. It has the highest risk of calcification among human organs and is not safeguarded by the blood-brain barrier. Tan et al., furthermore, proposed that the calcification of pineal gland can affect its function related to overall human health, the aging process, and melatonin production (a vital factor to many neuropathogenesis) (Tan et al., 2018). High fluoride accumulation ($\geq$50 mg F kg^{-1} pineal gland) showed a positive correlation with the pineal calcification in Thailand (Tharnpanich et al., 2016). Similarly, a study conducted in the UK found a positive correlation between the pineal fluoride level and the pineal calcification (Luke, 2001). This study also indicated that the F/Ca ratio in the pineal gland was exceedingly higher than that in corresponding bones, although no correlation found between the pineal fluoride and the bone fluoride levels.

4.3.6. Reproductive system fluoride toxicity

Various investigations have shown that fluoride has adverse effects on the reproductive organs and have attempted to understand its mechanism. NaF exposure structurally impairs the ovaries and uteri characterized by abnormal changes in weight and inhibits important steroid hormones for reproduction (i.e. estradiol, testosterone, and progesterone) (Zhou et al., 2013). However, the mechanism of aberration in weight is still indeterminate.

In the same way, the ability of fluoride to cross blood-brain barriers affecting pituitary gland and hypothalamus (controlling other hormone glands) has been suspected to further disrupt the reproductive function. Thus, the neurodegeneration due to fluoride exposure can apparently affect the reproductive function. The study also revealed that NaF can also inhibit follicle stimulating hormone (FSH) and luteinizing hormone (LH) (hormones responsible for the growth and stimulation of reproductive organs) from the pituitary gland (Zhou et al., 2013).

In 2015, a prevalence study among Chinese women provides initial evidence of the hypothalamus-pituitary mechanism on reproductive function. The study revealed that increased follicle hormone receptor caused a gene polymorphism on female reproductive hormones (Zhao et al., 2015). Correspondingly, Dhurvey et al. substantiate this initial finding suggesting that the decline of ovarian follicles is due to the fluoride-induced gonadotropin-releasing hormone (GnRH) inhibition supporting other previous studies (Dhurvey et al., 2017). The GnRH from the hypothalamus is a key neuropeptide which signals the release of FSH and LH from the pituitary gland. Moreover, traversing with the hypothalamus-pituitary-thyroid axis, the authors also revealed that atretic follicles and (tumor-linked) interstitial cell build-up can also be stimulated by hypothyroidism.

Meanwhile, Han et al. revealed that the connection to the hypothalamus-pituitary-testicular axis to reproductive impairment is just secondary (Han et al., 2015). Recent laboratory studies explain the possible mechanism of the reported reduction of male fertility due to NaF exposure. Wei et al. observe that after exposure, there is a reduction in sperm count and exorbitant aberration in the quality of sperm. (Wei et al., 2016). They further suppose that like the observed inflammation (an indicator of toxic exposure and damage tissue during pathogenesis) from previous NaF toxicity studies, the testicular inflammation can possibly exacerbate infertility due to testicular impairment. Zhang et al., similarly, reported that NaF causes testicular impairment characterized by defective autophagy with aberrant and excessive apoptosis (Zhang et al., 2016). In addition, Leydig cell (or interstitial cell), an essential cell that produces testosterone, can be inhibited by NaF (even at low levels, 1 ppm) through inducing cytotoxicity and reducing its viability and proliferation (Orta Yilmaz et al., 2018). These findings show pathological evidence indicating fluoride inhibition of reproductive function.

5. Discussion

5.1. CE in the context of SD

One of the principal issues of CE and SD is bridging the gap between theory and practice. In the analysis of recent CE reviews, it shows that there is a noticeable lack of consensus in the definition of CE in the literature (Homrich et al., 2018; Kirchherr et al., 2017; Korhonen et al., 2018b). This gap at the level of theoretical viewpoint is a clear impediment to achieve a smooth application of CE principles. Moreover, the earlier links between CE and SD is disregarded in recent literature. The most recurring definition of CE in the literature is “closed-loop”, “business model” and “supply chains” creating an intrinsic bias to just the economic aspect of SD. An example to this is the study of Suarez et al. formulating a standard optimizing material flow only within the supply chain and claiming to fill the gap of theory and practice in the context of SD (Suárez-Eiroa et al., 2019).

On the contrary, Boulding initially proposed a general perspective of the earth “as a closed system with the limited assimilative capacity and the co-existence of environmental protection and economic gain must be balanced” (Boulding, 1966). This perspective also stimulated the development of SD and different school of related-thoughts. Although the idea of the “closed system” remained intact, the initial objective is not limited to a “business model” or just economic aims. In this review, we reiterate the definition of CE as a tool for SD with the same three key objectives as SD. In other words, we suggest eluding from the closed-system business model (i.e. supply chain, closed-loop, etc.). This will help in restoring the aim for three key aspects of SD and in encouraging more multi-disciplinary participation in the development of CE.

The “supply chain” and “closed-loop” perspectives come from the aspiration to flee from the current “end-of-life” trend focusing on the eminent economic potential. However, this perspective terminates in the “disposal stage” and does not transcend to further exploration of the benefits to the environment and the society. At present, disposal methodologies do not guarantee complete environmental protection. These can inhibit contamination but only to slow down the process. Furthermore, the enclosed viewpoint of the supply, only focus on economic gain and misses to fill the gap within the relationship of CE to other SD objectives.

In addition, although, the three key aspects is restored, the conventional illustration of understanding SD creates friction between its three key aspects. Consequently, we proposed a theoretical “synergistic perspective” of SD. We further provide links between the three dimensions of SD by using terms such as “symbiosis”, “reciprocity” and “productivity”. In this way, the terms connote networks (or link critical to attaining a perpetual SD) within the three key dimensions making it beneficial vis-à-vis to each other. Narratives from the past decade also discussed “green economy”, “market sharing”, and “inclusive sustainability” generating a positive association between the three key aspects (Campbell, 2013; Ene et al., 2008; Larson, 2018).

Alternatively, Flynn and Hacking explained that CE cannot fully function without completely identifying key actors (i.e. standards, government, and market) and providing a win-win solution (Flynn and Hacking, 2019). Likewise, Ghisellini et al. encourage the participation of all actors to generate effective relationship and holistic standards (Ghisellini et al., 2016).

To attain the optimum potential of CE principle, continuous research technological development is necessary to overcome remarkable challenges in pursuing CE. Allwood recognized that unless a technological breakthrough happens which can disintegrate complex structure, complete waste elimination is not feasible (Allwood, 2014). Thus, secondary production from CE cannot sustainably replace primary production. In addition, the recycling process also requires energy (releasing emissions) which can also be unsustainable and result in more environmental damage (Korhonen et al., 2018a).

At the same time, the market is mostly controlled by private businesses. Geisdoerfer et al. remarked that the private sector will play a key role in having more resources and the ability to direct the other steering actors (Geissdoerfer et al., 2017). Market sharing, a recent development initiated by private sectors, helps to provide cheaper resources and services as an alternative and to benefit the marginalized communities (Nica and Potcovaru, 2015). For the implementation, the government and the policymakers should complement the initiatives of the private sector. The government will have the responsibility to orchestrate or control the movement towards CE and SD and to increase the public awareness encouraging participation. However, Millar et al. specified that the government is lacking coordination and not identifying the specific role, further inhibiting CE implementation (Millar et al., 2019). Stricter environmental standards and tax incentives should be implemented. These can create business opportunities and economic advantage while providing environmental protection (Ghisellini et al., 2016). In addition, environmental degradation has a domino effect that a decline in environmental health also affects human health. Remoudou and Koundouri further suggest that policies on the environment and public health should closely interrelated (Remoudou and Koundouri, 2009). They further proposed to quantify this environmental and social cost (which is still lacking and very hard to attain) to justify economic benefits.

We summarized in Fig. 4 that CE is just a node in the web of various and complex nodes (such as technology, law, market, government, nature, public health as a few of the steering actors) affecting SD objectives. The primary objective of CE is to realize a holistic approach resolving issues on sustainability and stimulates a

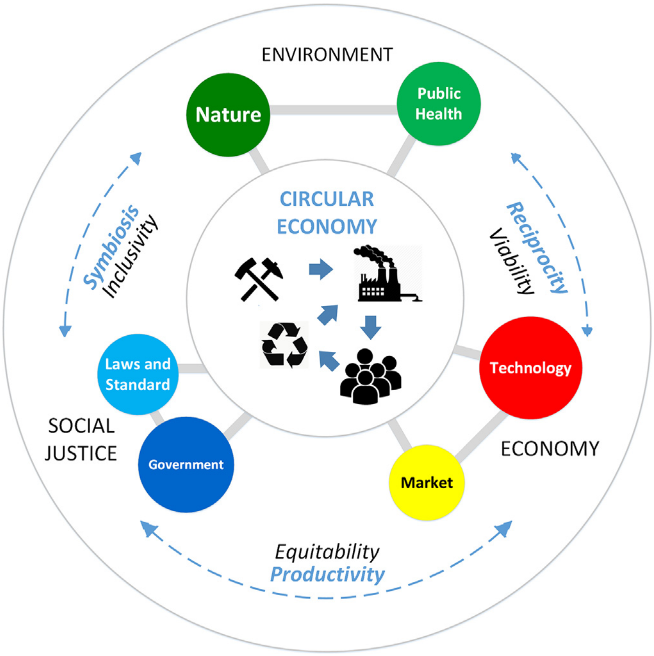

Fig. 4. Proposed CE Model: CE as a tool of SD, presented not just an “isolated close loop” as presented in the previous literature rather a node in a network forming web of different nodes, necessary for the attainment of SD objectives.

sharing economy among stakeholders (Naustdalslid, 2014). Thus, we suggest a departure from to the “closed-loop” or “end of life” perspective of CE through identifying the “steering actors” or “stakeholders” and through the formation of functioning linkages to attain SD. In addition, we propose that CE as a tool of SD should also incorporate the objectives of the three key dimensions of SD.

5.2. Fluoride existing life cycle

After the review of fluoride literature, the prevalent life cycle suggests a LE model posing a serious risk to the environment and human health as discussed in the previous sections. Illustrated in Fig. 5 are the observed fluoride life cycle and environmental fate and transport. Considerable amounts of fluorides are released as industrial by-products or effluents emitted into air or wastewater streams. Although these fluorides levels are reported and can significantly affect health and environment, information on the amount of fluoride waste streams at different phases in a global scale is still limited.

Moreover, artificial fluoridation a critical pathway of fluoride providing industrial fluoride to be redirected to more beneficial use with apparent economic benefits. Thus, some fluoride in its life cycle can be considered under the reuse economy. On the other hand, impaired sewage networks can also generate pollution through leakages not only for fluoride but also with its other contaminants.

Literature in Section 3.3.3 shows that developments on fluoride treatment depend on incineration-landfilling disposal of hazardous fluoride. However, these present methodologies do not guarantee absolute confinement and consequentially reintroduce contaminants back to the environment requiring further development of technology. The current methodologies are just considered to slow down its re-entry to the environment. At present, fluoride recovery in both practice and technology is still limited and further investigation on fluoride recovery processes is still essential and a continuous challenge to sustainability. However, it is emphasized that this disposal mechanism is not sustainable with the growing waste volume especially in the developing countries (Orlu et al., 2016).

5.3. Fluoride and SD

5.3.1. Defining fluoride

Besides technology, regulatory bodies play an important part especially in defining the character and parameters of fluoride. The regulation on fluoride, especially in drinking water, can still vary from different countries to different agencies. Likewise, this is also similar for the standards for effluents and environmental levels. In public health, there are also different perspectives on fluoride considering human health from “non-nutrient”, to “micronutrient”, to “essential nutrient” (EFSA, 2013). Recent literature shows that there are constant investigations on both adverse and beneficial

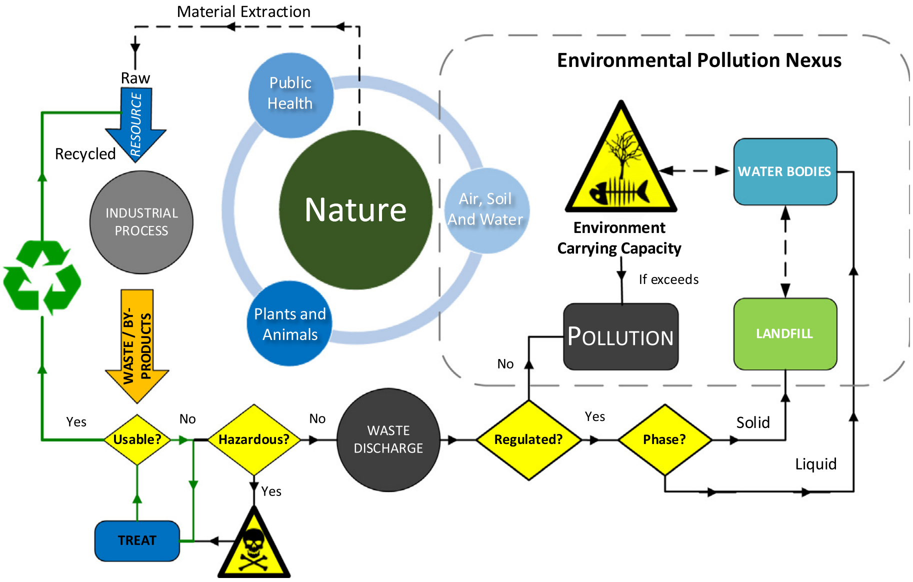

Fig. 5. Fluoride life cycle and environmental fate and transport.

health impacts, an indication of growing interest among researchers. Although the conventional use of fluoride-contained dentifrice just poses a minor risk, the utilization of municipal fluoridation is a critical pathway for fluoride, appealing for further and thorough investigations for policymaking. A well-shaped definition of fluoride health impacts can consequentially give a clearer grasp to the problem and will provide more identifiable objectives.

5.3.2. *Current fluoride LE to CE*

From the analysis of literature, a shift from the existing LE to CE has great potential. CE as a tool for SD must not only deal with economic stability but must also involve in environmental protection and social equity (Millar et al., 2019). Although, the economic gain is commonly the prior reason to CE, highlighting the environmental and social benefits can provide momentum pursuing CE.

Maintaining public health can also be considered an essential node in the web under the social aspect. As discussed in Section 4.3, fluoride can cause severe health distress affecting public health and further has some impacts on macroeconomics. As provided in previous sections, environmental degradation due to fluoride can affect both plants and animals also influencing live stocks, agriculture and aquaculture, providing economic and environmental linkages. Thus, environmental protection should not only understood as a mere expenditure but also an asset which can benefit the economy in general. Moreover, scholars from previous decades have already discussing poverty-environmental-deterioration nexus which web linkages cannot be denied (Duraiappah, 1998). Environmental deterioration can affect public health which commonly has a direct impact especially for the poor making it not only environmental but socio-economic issue. Moreover, the decline in the quality of public health worsens the untapped labor force of a country.

Lastly, artificial municipal water fluoridation is a complex issue and a critical node in the fluoride network involving various considerations. The re-utilization of fluoride from industrial by-products can explicitly provide economic gain. However, we believe that the municipal fluoridation does not completely reflect the principle of CE. First, although, fluoride can be retrieved from industrial by-products fluoride pathway, it ultimately ends to disposal making it under reuse economy. Moreover, water as nature's transport media can extensively distribute fluoride (e.g. agriculture, food, and beverages).

Second, fluoridation may undermine social justice (a key dimension of SD) due to ethical issues and apparent disregard for the poor. Artificial fluoridation is primarily executed for underprivileged communities without access to dental care. However, insufficient understanding can further ignore its primary objective to help the poor. From literature, the numerous fluoride fate in the human body and the severity of fluoride causing disease suggest that fluoridation increased health risk due to the increase in exposure to fluoridated water. However, resource governance is not only developing of advanced resource flows but must also include comprehensiveness of different aspect (Flynn and Hacking, 2019). Thus, in perspective of CE, we recommend a shift from artificial fluoridation to other fluoride utilization.

As previously discussed in Section 5.1, technological developments will still play a vital role. Improvement of material recovery technologies for fluoride will still be an emerging challenges since most of the recent developments still focus on fluoride disposal. Moreover, the considerations for further application must be all-inclusive, deliberate, and aligned in SD principles. To achieve this, the decision-makers should create strong and mutual linkages among different steering actors.

6. Conclusion

Although high levels of fluoride may occur naturally, anthropogenic activities accelerate its dispersion and may further aggravate its effects. The recent fluoride advancements are still far from the attainment of the CE principles. However, the prevalent CE considerations must also be comprehensive for the attainment of SD. Recent studies claimed that there is still a weak bond in applying CE theories into practice. From the review of the CE literature, it shows that CE tends to incline into a one-dimensional objective neglecting other dimensions of SD. Thus, to add a momentum aiming a perpetual CE, linkages between different dimensions of SD are proposed. Moreover, mapping out the pathways of specific material gives a clearer understanding and potential benefits of CE bridging a small gap between the theory and practice. In this review, we have mapped out fluoride pathway and the topical literature are still focusing on technologies for disposal characterized by LE. Nevertheless, there are also a few literature describing fluoride recovery which is promising in aiming CE principles. Furthermore, knowing the fate and transport of fluoride can help to modify the prevalent LE model to the CE model. The transition from LE to CE is understood to gain benefits in the different aspects of SD. In addition, the municipal fluoridation (a controversial practice and a critical network of in fluoride pathway) can be avoided but recognized to provide economic benefit. However, safer alternatives are recommended. Finally, CE is a promising alternative to attain environmental protection, economic growth and social equality which still requires both technological and institutional developments. As a recommendation having developments in the understanding of fluoride toxicity and a closer review of the policy regarding fluoride standards are viewed essential.

Declaration of interest

None.

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