Tin Stabilizers in Drinking Water

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Drinking Water Contaminants – Chemistry, Toxicology and Greener Interventions

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List of Abbreviations

PVC - Polyvinyl chloride

CPVC - Chlorinated polyvinyl chloride

HDPE - High-density polyethylene

OBS - Organic-based stabilizers

DAU - 3-dimethyl-6-aminouracil

BA - Barbituric acid

TBA- Thiobarbituric acid

Executive Summary

This report addresses the issue of tin stabilizers contaminating drinking water. Organotin compounds have been found to leach from polyvinyl chloride (PVC) pipes into drinking water. These organotin compounds originate from tin stabilizers that are used in the production of PVC products. Though there are other forms of PVC stabilizers, tin stabilizers are the most widely used stabilizers in North America. PVC stabilizers are used due to their ability to absorb HCl and prevent degradation of PVC. The leaching of organotins into drinking water is a concern due to the health impacts that they potentially pose for humans. This report examines common tin stabilizers and how they may break down in the drinking water environment. Tin stabilizers and the compounds that they break down into are assessed for their health impacts. The primary form of toxicity that tin stabilizers are known to have on humans is immunotoxicity; however, toxic effects of tin stabilizers are still not well understood. Some forms of organotins are found to cause neurotoxicity in humans, and can even lead to death in cases of high exposure. Therefore, the unknown health hazards associated with tin stabilizers may be of high concern.

Three interventions are considered as potential solutions to the issue of organotins leaching into drinking water in PVC pipes. The first potential solution is to intervene at water treatment plants by implementing water treatment systems that are effective in organotin removal. The second solution is to use alternative stabilizers for the production of PVC pipes. The third solution is to create regulations or guidelines regarding the use of tin-stabilized PVC. This solution can take the form of regulations against the use of tin-stabilized PVC for all drinking water distribution pipes or only post treatment pipes. This could also take the form of a regulation requiring a "first flush" of tin-stabilized PVC pipes, reducing the concentration of organotins in the drinking water.

Each of the solutions are analyzed based on how early they intervene, how effective they are in the removal of tin from drinking water at its end use, and their ability to be implemented. Water treatment technologies are effective in the removal of tin. However, tin can be leached into drinking water post-treatment. Drinking water treatment is considered to have a late point of intervention, moderate removal ability due to the reintroduction of tin, and low difficulty of implementation. Alternative stabilizers are considered to have an early point of intervention, high removal ability (as tin stabilizers will not be used), and moderate to high difficulty to implement, due to their disruption of the tin stabilizer industry. Regulatory solutions have ranging effectiveness depending on which regulation is implemented. A regulatory solution against the use of tin stabilizers for all drinking water pipes was found to be the most effective as it has an early intervention point and high ability to remove tin. However, it also would have a moderate to high difficulty to implement. Overall, the most appropriate solution was chosen to be a combination of the second and third solution. It is recommended that the use of alternative stabilizers be implemented in all drinking water pipes through the use of regulations. This solution may be difficult to implement due to its disruption of current practices and the tin stabilizer industry. However, it would be the most effective solution as it intervenes early and entirely removes the risk of organotins entering drinking water.

Abstract

Organic tin compounds have been found to leach into water from polyvinyl chloride (PVC) pipes used in drinking water distribution systems. These tin compounds pose potential health risks to humans. Solutions to help reduce human health risks have been identified and include: targeted drinking water treatment, use of alternative compounds in PVC manufacturing, and imposing regulations to prevent or reduce levels of organotin compounds present in drinking water. The most effective solution to this problem is identified to be a combination of regulations and the use of alternative stabilizers in PVC. This solution will prevent organotin compounds from leaching into drinking water and being consumed by humans.

1.0 Introduction

Tin compounds are a common drinking water contaminant, and pose potential risks to humans and the environment due to their toxicological properties. Potentially harmful tin compounds are present in water due to anthropogenic processes, and there may be opportunities to alter or introduce new processes to address this issue. One particularly large function of tin compounds is for use as PVC stabilizers in drinking water pipes. This poses potential health hazards to humans that are consuming water after it has travelled through PVC pipes.

The objectives of this report are as follows:

1. Determine common tin compounds that leach from PVC pipes,
2. Establish which form of tin compounds are present in drinking water,
3. Assess their specific concerns to humans, and
4. Propose solutions to address the issue.

2.0 Background

Tin compounds are used as heat stabilizers in plastics to prevent heat degradation [1]. Heat degradation primarily occurs during the processing stage of plastics [1]. However, it can also occur during the useful life of plastics [1]. The largest use of heat stabilizers is by far in PVC products, as PVC has a higher susceptibility to heat degradation than other plastics [1]. Heat stabilizer use in PVC plays a double role by preventing degradation and allowing for PVC materials to be recycled [1]. This is because the recycling process requires PVC to be heated to high temperatures [1].

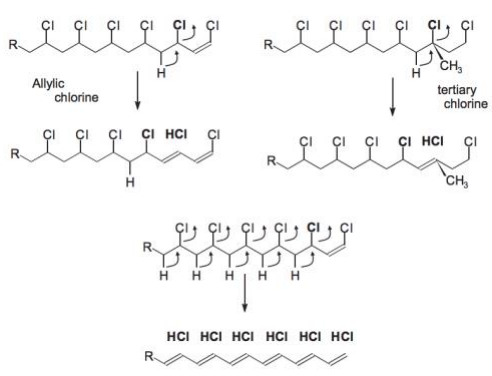
PVC is an extremely versatile material and is relied upon in many different industries [2]. The natural resources required to create PVC are natural salt and natural gas, which are inexpensive and abundant resources [3]. Natural gas is widely used around the globe, and will likely remain a resource that is abundantly extracted for use in industries other than plastic. Chlorine is a co-product in the manufacturing of sodium hydroxide through the use of natural salt [4]. Seventy million tonnes of sodium hydroxide and 44 million tonnes of chlorine are produced worldwide annually [4, 5]. Approximately 30% of chlorine production is used for PVC, and the availability of this resource is likely to remain high due to the valuable and inexpensive production process [5]. As a result, PVC is likely to remain prominent in the built environment.

The predominant use of PVC is in the construction sector, largely due to the cost-effectiveness it provides [6]. PVC has a comparatively low cost associated with production, transportation, installation, and maintenance or replacement [6]. Some applications of PVC, such as pipes, provide a potential in-service lifespan of up to 100 years [6]. This is crucial for construction components such as pipes, which are costly to access for maintenance [6]. Additionally, PVC products require less energy and resource use throughout their entire lifecycle when compared to traditional materials used in the construction industry [6]. For example, PVC pipes prevent leaks and have a smooth surface, reducing costs required for pumping water [6].

The use of PVC materials can result in contamination of drinking water with tin compounds. This is because PVC materials have a tendency to leach tin stabilizer compounds into the surrounding environment [7]. This occurs in PVC pipes used for conveying drinking water. A variety of different forms of heat stabilizers can be used in PVC pipe applications. The global use of heat stabilizer compounds is quite variant [8]. North America primarily uses tin stabilizers in PVC pipes [8]. However, other continents typically use alternative heat stabilizers, such as lead-based compounds [8].

2.1 Industrial Function of Tin Stabilizers

Tin stabilizers are widely used in PVC applications due to their beneficial properties for industrial processing, final product performance, and final product appearance [9]. Tin stabilizers are important in the production of PVC due to the high heat and stress imposed on PVC products [10]. At temperatures above 170°C, PVC releases HCl which starts an autocatalytic process and accelerates the release of more HCl [11]. This process of HCl production creates unstable molecular structures and leads to the decomposition of the PVC material [11]. Figure 1 displays the break-down of PVC to form HCl. Heat stabilizers are required to minimize this degradation by reacting with excess HCl to prevent the autocatalytic process from commencing [10]. Heat stabilizers in PVC can also enhance resistance to daylight, weathering, and heat aging [11]. There are a variety of alternative heat stabilizers; however, tin stabilizers are the most effective [10]. They have been used in the processing of PVC and CPVC products since the 1960s [10].



Formula 1.2 Degradation of PVC at allylic and tertiary carbon atoms due to heat or shearing

***Figure 1**: The release of HCl due to the degradation of PVC [12]*

Tin stabilizers are most commonly used in plastic pipes [13]. Approximately 375,000 tonnes of heat stabilizers were used in plastic pipes globally in 2017 [13]. The demand for these stabilizers is expected to remain prominent. According to a 2015 study, the global market for PVC heat stabilizers is expected to be USD 3.8 billion by 2020 [13]. The global demand for tin stabilizers specifically is expected to be 231,000 tonnes by 2025 [13]. The manufacturing of PVC stabilizers occurs in many countries worldwide. Several of the largest PVC stabilizer manufacturers are located in Germany, Japan, and the USA [13, 14, 15]. Many tin stabilizer manufacturers are located in China [16].

In North America, tin is used as a heat stabilizer for almost all PVC applications [17]. In Europe, tin stabilizers are mainly used for rigid, transparent PVC that undergoes rigorous processing conditions and requires further stabilization [17]. Tin stabilizers are approved for the use of potable water pipes in all European countries and North America [18]. However, North America is the only continent where tin stabilizers are the dominant stabilizers used in PVC pipe applications for potable water [17, 18]. In Canada, there are approximately 30 facilities that use tin stabilizers in the production of rigid vinyl (PVC and CPVC) products [10]. Figure 2 shows the use of different types of heat stabilizers across the globe. This figure illustrates North America's tendency to use tin stabilizers, while other continents predominantly use lead or calcium/zinc-based stabilizers.

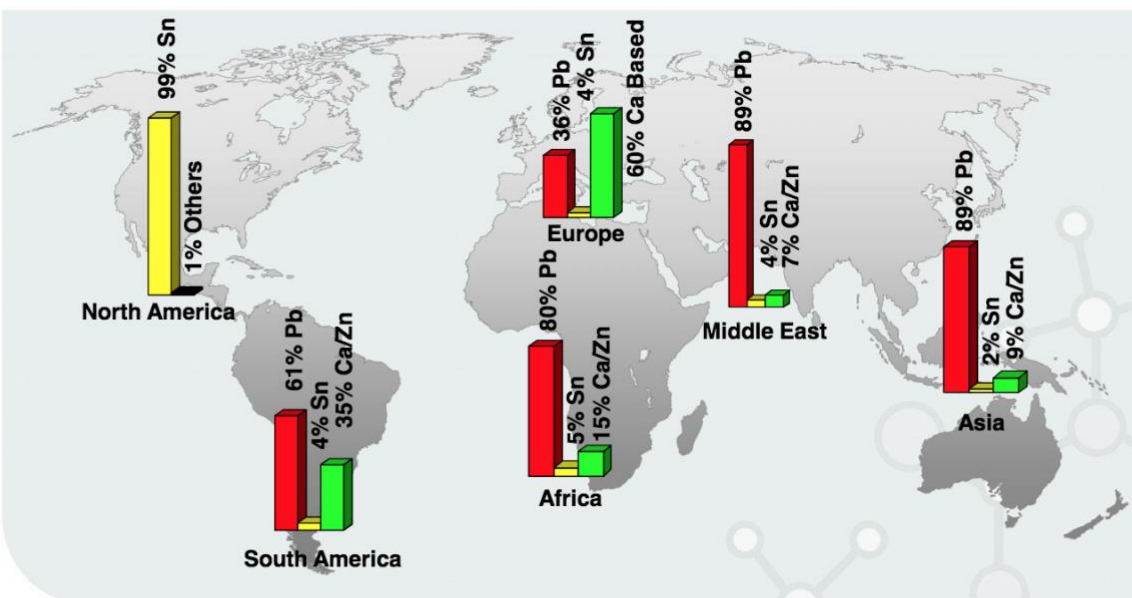


***Figure 2**: Heat stabilizer use around the globe [8]*

2.2 Life Cycle

As previously mentioned, tin stabilizers are commonly used in North America for the production of PVC materials [17]. A large portion of PVC is used for the production of PVC pipes [19]. Therefore, the research focus of this report is around the use of tin-stabilized PVC for the conveyance of drinking water, and how tin may enter the drinking water. Figure 3 outlines the life cycle of tin stabilizers with relation to drinking water systems.

As seen in the figure, tin stabilizers are manufactured and then used in the manufacturing of PVC materials, including PVC pipes [13]. These pipes are then used for drinking water conveyance from the water source to the drinking water treatment plant, and then from the plant to the end user. At the end of their useful life, PVC pipes are assumed to be disposed of in municipal landfills. Sludge from water treatment plants that may contain tin stabilizers may also be disposed of in landfills. However, there is currently a voluntary Canadian guideline which recommends that waste containing tin stabilizers is not disposed of in municipal landfills [10].

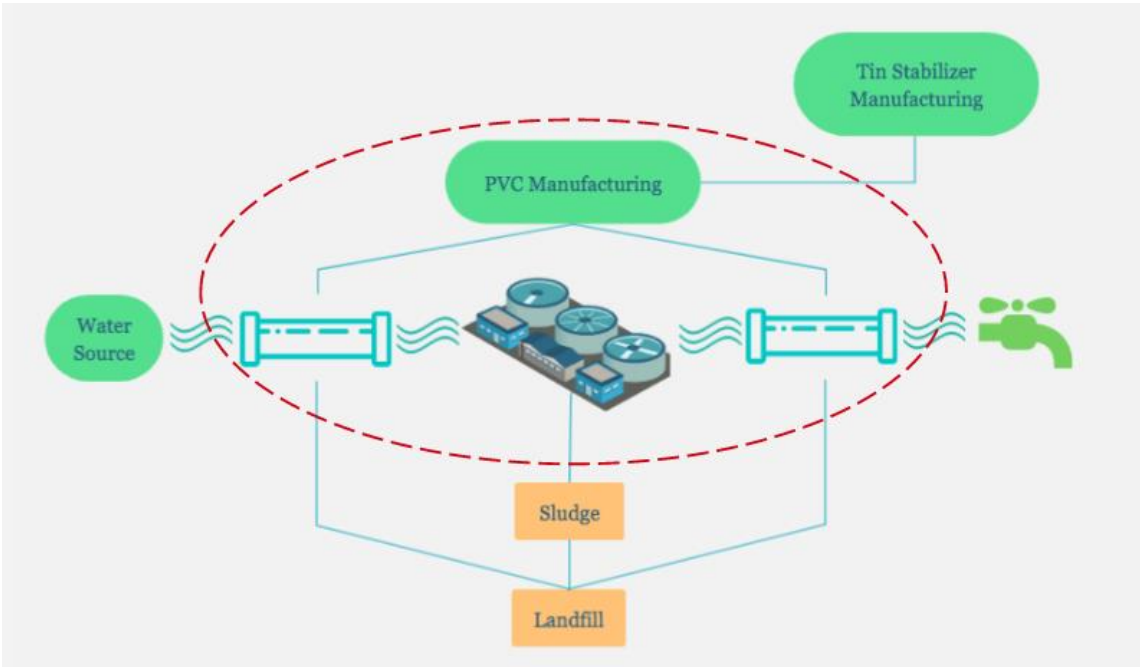


***Figure 3**: Life cycle of tin stabilizers in relation to drinking water*

For research purposes, a boundary was set to exclude tin that enters drinking water through contaminated water sources, leaching from tin stabilizer manufacturers and leaching from landfills (see Figure 3). The water source quality was not considered as this is not directly linked to the issue of tin stabilizers. Any changes to current practices involving tin stabilizers would not address issues of water contaminated by mining effluent, antifouling paints, or other sources of tin contaminants. Therefore, water source quality was considered to be outside the scope of this report.

Due to the popularity of tin stabilizers in North America, this report assumes a developed country context. It is assumed that in a developed country, manufacturing processes would be well-controlled. Because of this, leaching of tin stabilizers from the manufacturers is not considered. Similarly, leaching from landfills is not considered as they are assumed to be well-controlled in developed countries. Landfills are also excluded from the scope as “little is known about chemical leaching of organotin compounds mobilized by degradation of PVC materials in dumping sites” [20].

Within the chosen boundary, this report only addresses the impacts on humans. Specifically, this report considers health impacts on humans who ingest or come into contact with tin-contaminated drinking water. Impacts of tin stabilizers on the environment and aquatic ecosystems are considered to be outside the scope of this report. However, studies on marine creatures are referenced to illustrate adverse health effects that humans could potentially be exposed to. Additionally, the end use of the drinking water is not considered. However, this does not mean that these are not issues that need to be addressed. This decision was made based on the research focus of drinking water, which more specifically relates to humans than to aquatic or environmental impacts.

Three interventions are considered in this report. The first point of intervention is at the drinking water treatment plant. The second point of intervention is at the manufacturing of PVC. This intervention point interrupts the use of tin stabilizers in PVC products. The final point of intervention is in the use of tin-stabilized PVC pipes for drinking water distribution systems. This includes both pre- and post-treatment PVC distribution pipes. These interventions points are shown in Figure 4. The proposed solutions to be implemented at these intervention points are discussed in detail in Section 3.0 of this report.

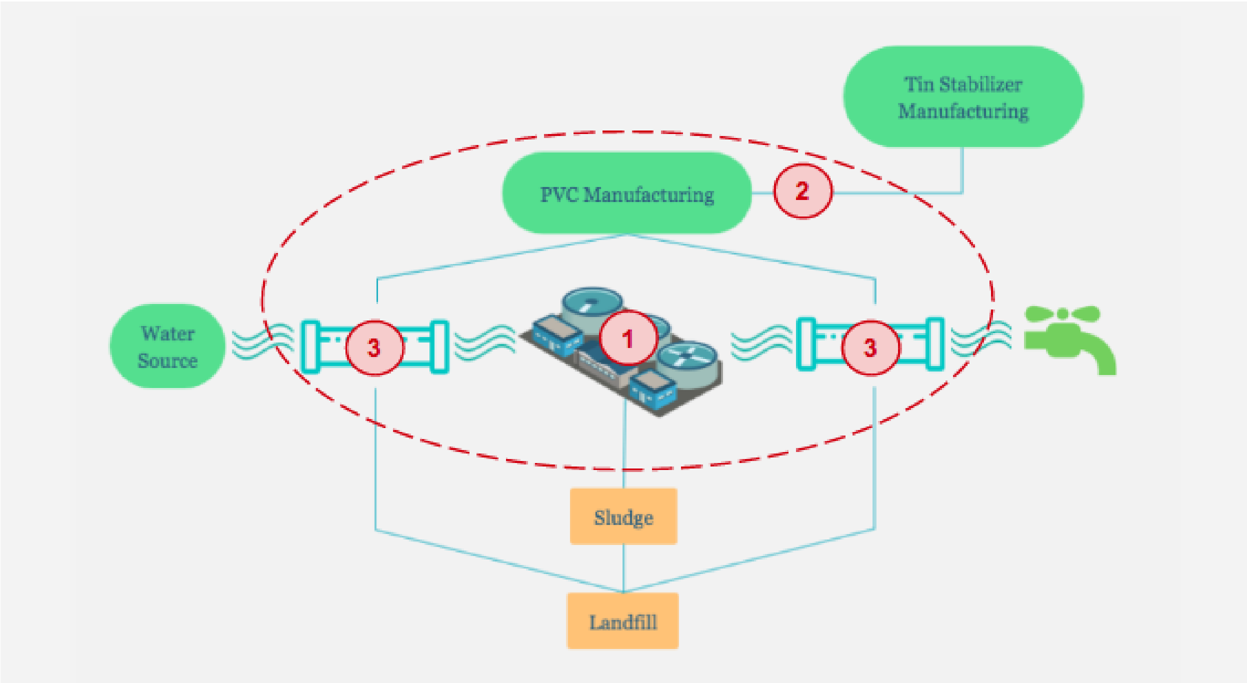


***Figure 4**: Points of intervention for the proposed solutions*

2.3 Speciation

As discussed in Section 2.2, this evaluation of tin contamination in drinking water is only concerned with PVC drinking water conveyance pipes as the contamination source. This will help determine the most harmful and abundant forms of tin that can be ingested by humans due to leaching of tin stabilizers from PVC pipes. In this context, an example of a common tin stabilizer used in PVC drinking water pipes is explored for its potential to break down in water after leaching from PVC.

Methyltin mercaptides are a family of organotin stabilizers commonly used for PVC drinking water pipe stabilization. A speciation diagram for a compound in this family, Dimethyltin Bis, can be seen below in Figure 5 [21]. A detailed explanation of this speciation diagram can be found in Appendix A. Methyltin mercaptides have not been found to leach from PVC products as intact compounds [21]. However, methyltin degradation products – such as monomethyltin and dimethyltin compounds – have the potential to leach from PVC pipes due to their high solubility in water [21]. Additionally, the organotin compounds typically found in drinking water distribution systems through testing are monomethyltin and dimethyltin [22].

The water solubility of organotin compounds is generally low, and they tend to adsorb to suspended particles in water [20]. Additionally, organotin compounds typically only degrade into inorganic tin compounds by exposure to UV light or certain bacteria [23]. Neither of these are likely to be present in potable water pipes after treatment. This indicates that dimethyltin and monomethyltin compounds will likely not degrade to significant concentrations of the inorganic tin compounds on the speciation diagram. The speciation diagram is focused on methyltin compounds. However, the same reasoning can be used to assume that other organotin stabilizers, such as di- and mono-butyltin compounds, will remain as organic compounds rather than break down to inorganic compounds.

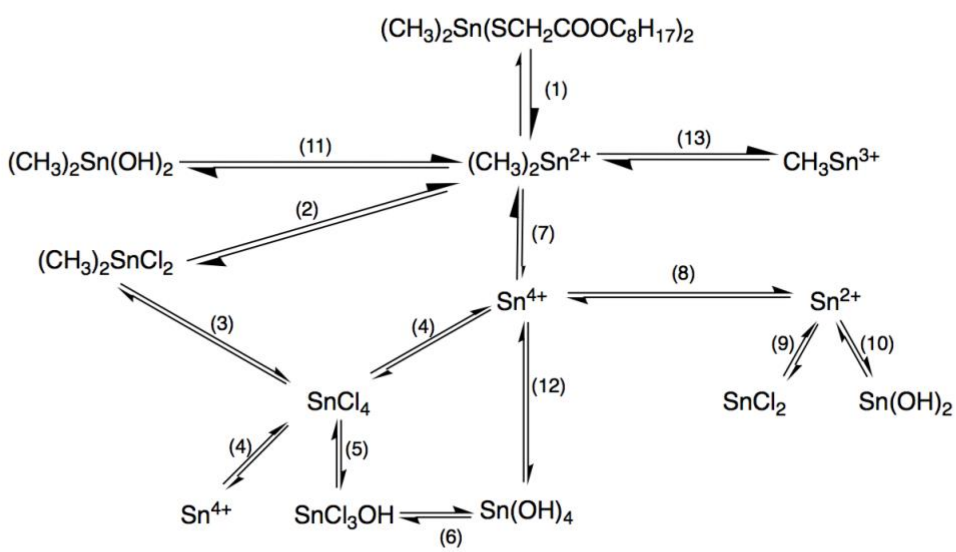


***Figure 5**: Speciation of Dimethyltin Bis in Drinking Water Pipes*

2.4 Toxicity

Generally inorganic tin compounds do not cause severely harmful effects [23]. This is because they can enter and leave the human body rapidly after being inhaled or eaten [23]. Alternatively, certain organotin compounds can cause harmful effects in humans [23]. As mentioned, organotin compounds are present in PVC-distributed drinking water. Therefore, their toxic effects are relevant for drinking water applications.

The World Health Organization states that the compounds that may leach from newly installed PVC pipes are primarily immunotoxins [24]. According to the National Toxicology Program, mono and di methyl and butyltins are the primary organotins present in drinking water [25]. Butyltins appear to be more toxic, but methyltins appear to have potential to cause neurotoxicity [25]. However, there is very limited data on these compounds, and the specific level of neurotoxicity of these compounds is uncertain [25].

NSF has established voluntary standards on the acceptable levels of several organotin compounds in drinking water [25]. These levels are 100 µg/L for short term exposure to mono and dimethyltin and mono and dibutyltin, and 30 µg/L for chronic exposure [25].

Many studies demonstrate that exposure to organotin compounds can be harmful, and several are referenced below. In each study, the exposure levels are higher than what is typically present in drinking water distributed through PVC pipes. However, the trends of severe health impacts should not be ignored. The capacity of organotins to bioaccumulate is uncertain [26]. If bioaccumulation were to occur, it might be possible for humans to face the adverse health effects that usually accompany higher exposure levels.

2.4.1 Human Toxicity

Direct exposure to organotins often causes insomnia and loss of memory in humans [27]. Exposure to trimethyltin in particular can cause neurotoxicity [28]. However, trimethyl exposure does not usually occur through drinking water [25]. Organotin exposure can also cause death in humans [27]. Workers who were exposed to a combined solution of dimethyltin and trimethyltin over 3 days for a total of 90 minutes experienced severe health impacts [27]. One worker was hospitalized, one died, and one was unable to return to work [27].

2.4.2 Rat Toxicity

The effects of organotins on rats were also investigated, since compounds that adversely affect rats typically also adversely affect humans [29]. Rats exposed to mono and di methyl and butyltin have experienced severe health impacts [25]. When pregnant rats were exposed to high levels of methyltin in drinking water, their pups displayed impaired learning abilities [30]. Rats exposed to a combination of mono and dimethyltin at 20, 100, and 500 ppm experienced renal and urinary bladder changes [30].

Pregnant rats exposed to 1.7 to 50 mg/kg/day of dibutyltin diacetate by gavage experienced decreased thymic weights [31]. The rats experienced decreased maternal weights at the highest dose [31]. Increased fetal mortality and malformations were experienced compared to control rats [31]. Pregnant rats exposed to 10 or 15 mg/kg of dibutyltin dichloride experienced decreased maternal weight gain, decreased fetal weights, and increased fetal malformations compared to control rats [32].

2.4.3 Marine Toxicity

Organotin compounds (mainly tributyltin) were previously used in marine anti-fouling paints [33]. Tributyltin can break down to other compounds, such as dibutyltin, in marine environments [34]. Butyltins are persistent and have an affinity for biological tissues [35, 36]. As a result, they are widely present in fish, mussels, snails, dolphins and seals [35, 36]. Organotin compounds can act as endocrine disruptors, causing imposex, intersex, and masculinization of shell creatures [37].

As a result of these adverse impacts, the International Maritime Organization decided to ban the use of organotin compounds for antifouling paints for marine vessels [37]. This ban began in 2003 [37]. Following this, Europe responded by not using tin compounds as PVC stabilizers [38]. However, as previously mentioned, North America continues to use organotin compounds as tin stabilizers.

3.0 Proposed Solutions

Our team proposes three solutions to address the issue of tin stabilizers entering drinking water. The solutions intervene at different points in the life cycle of tin stabilizers as discussed in Section 2.2. Each solution is researched for its effectiveness and feasibility. These solutions are compared to each other and the current practices to determine the most appropriate solution. The proposed solutions will be assessed based on their ability to:

- Address the issue of tin in drinking water at an upstream point;
- Reduce the level of tin in water at the point of use;
- Be implemented effectively.

The three proposed solutions are as follows:

1. Water Treatment Technologies,
2. Alternative Stabilizers,
3. Regulatory Solutions.

3.1 Water Treatment Technologies

The first solution is to intervene at drinking water treatment facilities. Conventional water treatment involves the processes of coagulation, flocculation, sedimentation, filtration and disinfection [39]. The conventional water treatment process is shown in Figure 6. These conventional processes do not specifically target the removal of tin. To intervene, this solution uses water treatment technologies that are effective at removing tin that has leached into the water. The focus for this intervention was the removal of di- and mono-alkyltin compounds. Alkyltin compounds are the forms of tin that are used as tin stabilizers, found in drinking water, and harmful to humans [7, 20, 40]. Our team researched the properties of alkyltin compounds to determine the best method of removal.

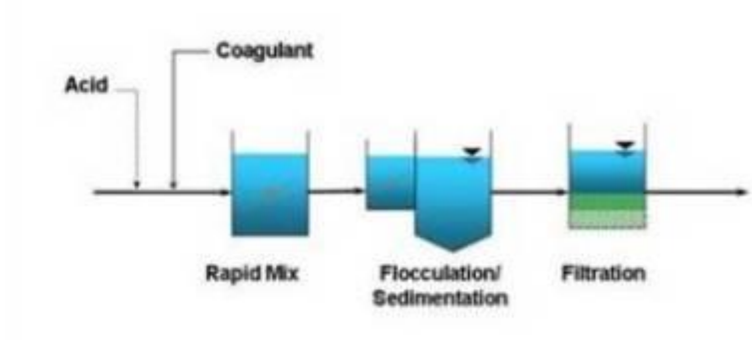


Figure 6: *Conventional water treatment process [39]*

Alkyltins have a high adsorption potential to materials such as soil with high carbon content [41]. Due to this potential, adsorption and flocculation is considered to be a suitable removal technology. The general process of contaminant removal by adsorption and flocculation is shown in Figure 7. The adsorbent is added to water which is then put through a rapid mix. This allows the adsorbents to attract and retain the unwanted compounds [42]. The mixed solution enters a flocculation and sedimentation basin where flocs can form and settle out of solution.

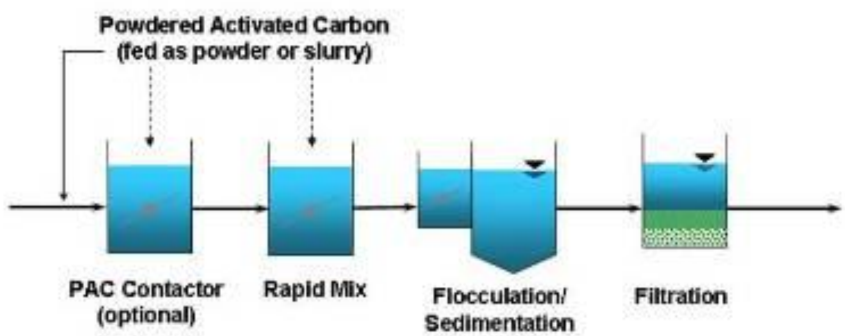


Figure 7: Contaminant removal by adsorption and flocculation using powdered activated carbon as the adsorbent [43]

Common adsorbents include bentonite, granular activated carbon, and powdered activated carbon [33]. A study compared the organotin and heavy metal removal of several adsorbents [33]. Powdered activated carbon was found to be the most effective adsorbent for the removal of organotins specifically [33]. When tested on a sample of wastewater containing 1000µg/L of organotins, powdered activated carbon was found to reduce the concentration by more than 99.98% [33]. This would reduce the concentration to 2µg/L, which is well below the level of 30µg/L recommended by NSF [25].

3.1.1 Water Treatment Technologies Limitations

Though the removal rates of adsorption and flocculation are sufficient, the use of this technology has limitations. It has no effect on the water after it leaves the treatment facility. A study was done on Canadian households that received drinking water through a PVC water distribution system [44]. The study detected levels of methyltin compounds in the water at 10 out of the 22 households sampled [44]. The concentrations of mono-methyltin ranged from 0.5ng/L to 257ng/L [44]. The concentrations of di-methyltin ranged from 0.5ng/L to 6.5ng/L [44]. These levels were detected at the households despite there being no organotins detected in the water leaving the treatment plant [44]. This suggests that although adsorption and flocculation is an effective removal technology, it is not an ideal solution if organotin compounds will be reintroduced into the system post-treatment.

3.2 Alternative Stabilizers

The second solution is to use alternative heat stabilizers. This solution addresses the manufacturing intervention point, and is concerned with replacing the tin compounds currently used as stabilizers in PVC. Intervening at the manufacturing point in the life cycle flow of tin stabilizers is the only proposed solution that prevents the contamination of drinking water with tin compounds. Reactive solutions, such as drinking water treatment, are no longer required if the use of tin compounds in PVC is prevented.

A variety of alternative stabilizer compounds exist for PVC pipe applications. Historically, the most commonly used heat stabilizers for PVC pipes have been toxic heavy metals such as lead and tin [8]. The recent worldwide increase in environmental consciousness and human health awareness has turned attention in the PVC industry to non-toxic and environmentally friendly heat stabilizers [45].

3.2.1 Calcium/Zinc Stabilizers

Calcium/zinc stabilizer systems are not new in PVC applications, as they have been in use for over 25 years [46]. Europe has standardized the use of calcium/zinc stabilizers for a variety of applications, including potable water pipes [46]. This is largely due to the fact that all tin stabilizers were classified as toxic in Europe after a four-year testing program was conducted [18]. Following this program, necessary precautions were put into place to prevent humans from ingesting or absorbing tin stabilizers [18].

The compounds used in calcium/zinc stabilizing systems consist of calcium and zinc carboxylates and additional organic compound additives [47, 46]. Examples of these metal carboxylates that are commonly used include calcium stearate and zinc stearate [47]. The additional organic additives typically consist of polyols, epoxidized soya bean oil, antioxidants, and organic phosphites [46]. These compounds used in calcium/zinc stabilizer systems are non-toxic or have relatively low toxicity [46, 47]. When compared to tin stabilizers, there appears to be more certainty that low-toxicity forms of calcium/zinc stabilizers have lower potential to harm humans [48, 49]. Many of these stabilizing systems are approved for food contact use in Europe [46]. However, this is dependent on the specific co-stabilizers that are used; there are many co-stabilizers that have not yet been approved for food contact [46].

The heat stability that these compounds offer for PVC during production is not as efficient as the heat stability that tin compounds offer [46]. For this reason, additional additives, called co-stabilizers, are required to improve the performance of calcium/zinc stabilizer systems in PVC

[46]. These co-stabilizers help improve the color and heat stability, allowing the PVC to have an acceptable lifespan and acceptable performance [46].

3.2.2 Organic Based Stabilizers (OBS)

Organic based stabilizers (OBS) are a relatively new technology that provide non-toxic and environmentally friendly stabilization of PVC [50]. In recent years, organic based heat stabilizers have been a large interest for the academic community and the PVC industry [50]. PVC companies appear to be increasing efforts to produce or use OBS for PVC [51]. It is difficult to find PVC manufacturers' information on specific organic based heat stabilizers currently offered. However, a large amount of information on OBS is available in academic literature. Common examples of OBS that are well-documented in research papers include: 3-dimethyl-6-aminouracil (DAU), barbituric acid (BA), and thiobarbituric acid (TBA).

One study concluded that PVC that uses DAU outperforms PVC that uses traditional lead-based and calcium/zinc stabilizers in terms of flexural strength and thermal stability during processing [50]. Additionally, it was found that DAU provides PVC with greater recyclability and color retention than traditional heat stabilizers [50]. Abundant information on the toxicity of DAU is not available. However, DAU is an uracil derivative, and toxicity information on uracil indicates that its derivatives are likely not hazardous to humans [52].

Another study focused on the heat stability performance of BA and TBA compounds in PVC. This study concluded that PVC with BA or TBA exhibits greater heat stabilizing efficiency and color stability than PVC that uses lead-based, cadmium-based, and tin-based heat stabilizers [53]. BA and TBA are both non-toxic and thermally stable materials with high melting points [53]. Low confidence studies have concluded that a potential concern with BA may be acute irritation to human skin, eyes, and respiratory systems [54]. Research on TBA shows there are low toxicity hazards associated with issues around mutagenicity [55].

Based on the results of studies that have been conducted on the performance of OBS in PVC, it appears that the performance and recyclability of PVC pipes can be increased by using these alternative heat stabilizers. The abundant research available on the effectiveness of OBS in PVC implies that there is high potential that this technology will continue to increase in availability. Some companies have already gained approvals for the use of OBS in drinking water pipe applications [51]. Many more forms of OBS are researched and tested, showing promise for more discovery and availability of OBS products in the future [45]. The low or non-existent human health and environmental risks make OBS a potential solution for safe and environmentally friendly PVC use in potable water pipe applications.

3.2.3 Alternative Stabilizers Limitations

Alternative heat stabilizers in PVC appear to be a viable intervention to prevent harmful tin compounds from contaminating drinking water. However, there are still limitations associated with implementing this solution, and they should be noted for further consideration.

A considerable limitation associated with replacing tin stabilizers with calcium/zinc stabilizers is the need for co-stabilizers. The addition of co-stabilizers increases the complexity of PVC processing, and can increase costs of production due to additional materials being added to the PVC mixture [46].

OBS and calcium/zinc stabilizers have been in use for a shorter time period than tin and lead stabilizers [46]. OBS and calcium/zinc stabilizers have been used for approximately 25 years, whereas tin and lead stabilizers have been used for over 40 years [46]. This implies that there is less certainty on the lifespan of PVC that uses these newer stabilizers.

The fact that countries such as Canada do not currently classify any tin stabilizers as toxic substances [10] may lead to PVC manufacturing companies being misinformed on the toxicity of tin stabilizers. Regulatory action would likely be needed to make manufacturing companies replace tin stabilizers, as there are no regulations in place to force them to use alternative stabilizers [56].

3.3 Regulatory Solutions

The third solution is to introduce recommended guidelines or regulations for tin stabilizer use. This intervention could affect the manufacturing of PVC, the selection of piping materials, or the initial use of PVC.

The potential regulations that could be implemented are as follows:

1. Discourage the use of tin stabilizers in all drinking water conveyance pipes
2. Discourage the use of tin stabilizers in post-treatment distribution pipes
3. Require that all PVC pipes used for potable water applications undergo an initial flush before their first use.

3.3.1 Potential Regulation 1 – Discourage use of tin stabilizers in all pipes

The first potential regulation would prevent tin stabilizers from entering drinking water within all PVC pipes. A similar solution to this has been implemented in Europe. European countries classified all tin stabilizers as toxic in 2006, and have voluntarily stopped using them since then [18]. Canada does not classify most tin stabilizers as hazardous substances and uses them widely [10, 17].

3.3.1 Potential Regulation 2 – Discourage use of tin stabilizers in post-treatment pipes

The second potential regulation would prevent tin stabilizers from entering drinking water within water distribution pipes. As explained under Section 3.1, tin can be removed from drinking water at drinking water treatment plants. Once tin is removed at treatment plants, emphasis can be placed on preventing tin from re-entering water post-treatment. With this emphasis in place, it is less concerning if water becomes contaminated with tin in conveyance pipes prior to treatment. Therefore, conveyance pipes prior to drinking water treatment plants could still be made with tin-stabilized PVC.

For this regulatory solution to be beneficial, it would need to be implemented in conjunction with treatment that adequately removes tin from water. As discussed in Section 3.1, contaminant removal by adsorption and flocculation is an effective way to remove organotin compounds from water.

Assuming adequate water treatment technologies for removing tin compounds are already in place, this regulatory solution may be more practical to implement than the first potential regulation. If only post-treatment pipes need to be tin stabilizer-free, pipes that delivers water to treatment plants could continue to be manufactured according to current practices.

3.3.3 Potential Regulation 3 – Require First Flush for PVC Pipes

The third potential regulation enables the concentration of tin compounds found in drinking water to be reduced. A study has shown that flushing PVC pipes with water can greatly reduce the concentration of organotins in the water [20]. This study measures the concentration of organotins in water prior to flushing to be 30,000 ng/L, and during subsequent distribution to be 1000 ng/L [20]. Several other studies suggest that common organotin concentration ranges for water distributed through PVC pipes are from 0.5 - 425 ng/L [7, 40, 44]. These values are significantly lower than the 30,000 ng/L found during the first flush study. This indicates that significantly lower concentrations of tin leach from PVC throughout its lifetime than during its first use. Therefore, it would be beneficial to require that PVC pipes are flushed with water prior to being used for drinking water distribution.

3.3.4 Alternative Piping Materials

For either of the first two regulations to be implemented, alternative stabilizers or alternative piping materials would need to be used. Alternative stabilizers to tin are discussed under Section 3.2. Several alternative piping materials that could be used instead of PVC include ductile iron, steel, and high-density polyethylene (HDPE). Each of these piping materials are already used in North America [57, 58]. A high-level analysis of these different materials is shown in **Table 1**. The values and ratings in the table are generalizations made from several different sources. It should be noted that many of the available sources on relative ease of installation are biased, so the ratings in this category do not have a high level of certainty.

***Table 1**: Comparison of PVC to alternative piping materials [57, 58, 59, 60, 61, 62, 63, 64, 65, 66, 67, 68, 69, 70]*

Material	Expected Lifespan	Relative Ease of Installation	Relative Cost
Tin-stabilized PVC	50-100 years	Easy	Low
Ductile Iron	50-100 years	Moderate	Moderate
Steel	40-70 years	Challenging	High
HDPE	50-100 years*	Easy	High**

*HDPE has been in existence for less than 50 years, so its expected lifespan is based on projections rather than experience with the material.
**There is less pricing information available on HDPE than the other materials. Therefore the relative cost is less certain.

As seen in the table, several of the alternative materials have similar expected lifespans to PVC. However, steel is generally reported as having a lower lifespan [59, 60, 62, 63]. Regarding the relative ease of installation, PVC and HDPE are both rated as easy, because several sources suggest that plastic piping materials are easier to work with than metals [66, 67, 70]. HDPE may actually be easier to install than PVC in certain circumstances [58, 68, 69]. This is partially because it is a flexible material, and is therefore able to round corners without additional joints [69].

Ductile iron is rated as moderate, because as mentioned above, several sources suggest metals are not as easy to work with [66, 67, 70]. Steel is rated as challenging because the pipe sections may need to be welded together, which increases the difficulty of installation [71].

The relative material and installation costs of each of these other materials are generally higher than PVC [59, 64, 65]. This is likely partially due to chlorine being readily available for use [38], as discussed under Section 2.0. The availability of chlorine contributes to the low cost of PVC, since chlorine is one of the main constituents of PVC [38].

3.3.5 Regulatory Solutions Limitations

There are several limitations associated with implementing regulations to reduce the presence of organotins in water. There is limited data available on the hazards associated with tin stabilizers. This could make it difficult to implement regulations surrounding their use. If tin stabilizers are not proven to cause human health hazards, pipe producers will not feel obligated to stop using tin stabilizers. Additionally, the regulations do not address the tin stabilizers present in existing pipe networks. Unless all existing tin-stabilized PVC pipes are replaced, tin can continue to leach into drinking water through PVC pipes.

Using alternative piping materials to PVC presents several challenges. PVC is a commonly used piping material. If contractors are more comfortable working with PVC than other materials, switching to other materials might require additional training for laborers. In the case of HDPE, several sources suggest that HDPE pipes may be easier to install than PVC in certain circumstances [58, 68, 69]. However, there would be a learning curve as workers adapt to using any new material.

4.0 Analysis of Proposed Solutions

Each of the three potential solutions are compared based on their point of intervention, ability to prevent tin from being present at the consumption point, and ease of implementation. A summary of these comparisons can be found in Table 2. Points of intervention early in the life cycle are favorable because they address issues at the origin of the problem. The findings on potential toxicity of mono- and di-alkyl tin compounds suggest that the ability of a solution to prevent tin from being present at the tap is crucial. Ease of implementation is an important consideration as well, because it can be difficult to disturb processes underway in large industries.

Table 2: General comparison of the three potential solutions

Solution		Point of Intervention	Ability to prevent tin from being present at the tap	Implementation Difficulty
Water Treatment Technology		downstream	moderate	low
Alternative Stabilizers		upstream	high	moderate-high
Regulatory Solutions:	All pipe materials	upstream	high	moderate-high
	Post-treatment pipe materials	combination	high	moderate-high
	First Flush	combination	moderate	moderate-high

Water treatment technology is considered to be a downstream intervention because it removes tin compounds after they have entered the drinking water distribution system. Alternative heat stabilizers and regulatory actions are considered to be upstream interventions. This is because they prevent tin compounds from entering drinking water.

The solutions which avoid the use of tin stabilizers in PVC have a greater ability to prevent tin from being present at the drinking water consumption point. The solutions which attempt to reduce or remove tin compounds from drinking water are less effective in preventing tin from being present at the water consumption point due to leaching still occurring.

Ease of implementation is difficult to accurately assess without further industry knowledge and professional advice. However, it is clear that disrupting an industry as large as the PVC industry would not be easy due to political and economic constraints. The water treatment technology solution is considered to be relatively low difficulty to implement at treatment plants where coagulation and flocculation are already in place. At these plants, the only additional costs and changes in processes would be the addition of activated carbon products. Regulations and alternative stabilizers are difficult to implement due to the lack of conclusive research on the toxicity of tin stabilizers, as mentioned previously in this report. This leads to regulatory bodies having difficulty in establishing clear guidelines and restrictions. Manufacturers will not likely want to increase expenditures to change their practices if there is no regulatory pressure to do so. Table 3 compares all alternative materials and stabilizers that can be used to replace tin-stabilized PVC, with respect to performance, cost, ease of installation, and hazards.

Table 3: Comparison of PVC using tin stabilizers to alternatives

Material	Lifespan	Relative Ease of Installation	Relative Cost	Potential Hazards
PVC using tin stabilizers	50-100 years	easy	low	moderate
PVC using Calcium/Zinc stabilizers	50-100 years*	easy	moderate -due to co-stabilizers	low
PVC using organic based stabilizers	50-100 years*	easy	low	low
Ductile Iron	50-100 years	moderate	moderate	low
Steel	40-70 years	challenging	high	low
HDPE	50-100 years*	easy	high	moderate

*Material or stabilizer has been in use for fewer years than its stated lifespan; lifespans are based on predictions rather than experience.

Each of the alternative solutions identified in Table 3 have similar projected lifespans. As mentioned previously, HDPE and PVC with alternative stabilizers have both been in use for less than 50 years. Therefore, their projected lifespans may be subject to change as more experience is gained with these materials.

As mentioned in Section 3.3.4, PVC and HDPE are rated as easy to install, because several sources suggest that plastic piping materials are easier to work with [66, 67, 70]. Ductile iron is rated as moderate, because it is a metal. Steel is rated as challenging because it is a metal, and may also require welding, increasing the difficulty of installation [71].

As mentioned, the cost of purchasing and installing PVC pipes is less expensive than HDPE, ductile iron, and steel pipes. Regarding PVC stabilized with alternate stabilizers, tin stabilizers and organic-based stabilizers are assumed to cost the least. This is because they do not require co-stabilizers to help with heat stability. Calcium/zinc stabilizers require co-stabilizers to perform at acceptable standards, and consequently are expected to increase the manufacturing cost of PVC pipes.

As mentioned throughout this report, tin stabilizers pose potential human health hazards. A study on HDPE pipes suggests that there is also potential for toxic compounds to leach from HDPE into water [72]. Regarding ductile iron and steel pipes, iron and carbon are the primary elements used [73]. The World Health Organization has found that these materials also pose relatively low health risks when considering the amount of iron and carbon leaching in to drinking water [73]. As discussed in Section 3.2, each of the proposed alternative PVC stabilizers have lower human health risks than tin stabilizers. Some of the alternative stabilizers are not known to pose any human health risks.

In general, steel pipes, ductile iron pipes and PVC pipes using alternative stabilizers are assumed to have lower human health hazards than tin-stabilized PVC pipes. This is because the constituent elements of these alternative materials and stabilizers are more greatly present in organisms [74]. This point is illustrated in Figure 8, where it can be seen that tin is not as abundant in organisms as calcium, zinc, iron, carbon, sulfur, and oxygen – the primary constituent elements in the alternative pipes mentioned [74].

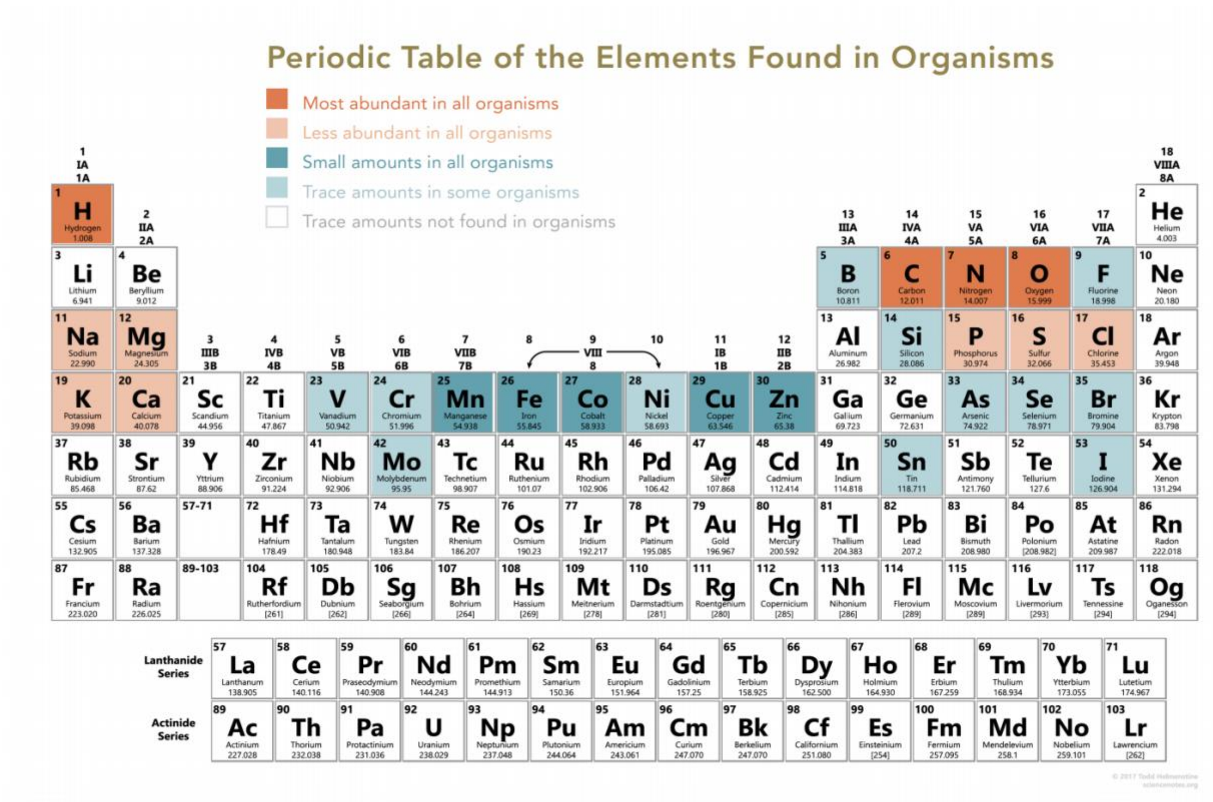


Figure 8: Periodic table showing elements found in organisms [74]

It should be noted that there is still uncertainty on the toxicity of the low concentrations of compounds that could leach in to drinking water from pipes. However, the findings discussed in this analysis suggest that the relative hazards to humans are as illustrated in Table 3.

5.0 Conclusion

The potential hazards of organotin contamination in drinking water are evident, due to the toxicity of organotin compounds and the large use of PVC pipes for drinking water conveyance in North America. Based on the proposed interventions, it is clear that there is not one specific solution that will solve this issue, but rather a combination of solutions that will help solve it. Water treatment is effective for the removal of harmful tin compounds. However, this solution does not address the issue of tin compounds continuing to leach into drinking water from pipes after it passes though the treatment plant. The use of alternative heat stabilizers in PVC pipes allows for the risks and uncertainty of tin stabilizers to be mitigated without discontinuing the use of PVC. Finally, introducing regulations appears to be an effective way to implement alternative stabilizers and prevent PVC potable water pipes from containing tin stabilizers.

Based on the analysis of solutions, a combination of regulations and organic-based stabilizers provides the most effective solution in meeting the objectives outlined in Section 3.0. Therefore, regulations should be implemented to encourage the use of organic-based stabilizers in all PVC pipes used to convey drinking water. This solution is an upstream intervention in the life cycle of tin stabilizers, as it prevents the use of organotins in the manufacturing of potable water pipes. Consequently, this solution removes organotin compounds from drinking water at the consumption point, greatly reducing any human health hazards. This solution is also expected to be feasible because it does not discontinue the use of PVC. It was found that PVC is inexpensive and easy to produce, making it an extremely important material in piping and construction projects. Although there are potential difficulties in implementing this solution, it appears to be the best solution for the problem at hand. Further research on the topic should address detailed implementation plans.

6.0 Recommendations

Based on the findings in this report, our team recommends that further studies are performed on the toxicity of tin stabilizers. These studies should specifically be on low concentrations of tin stabilizers and their ability to bioaccumulate in the human body. This would be useful in determining the exact health effects of tin stabilizers.

We also recommend further studies on the impacts of plastic disposal. As mentioned in Section 2.0, this report discusses tin stabilizer use in the North American context. Since landfills are typically well-regulated in North America, it is assumed that landfill leachate would not reach drinking water sources. As a result, it is also assumed that tin stabilizers would not enter drinking water from landfills. However, in locations where landfills are not regulated in the same way, such as in developing countries, there is greater potential for leachate to reach drinking water sources. Therefore, the impacts of plastic disposal in these regions should be assessed.

Additionally, the conclusions drawn from the drinking water treatment solution suggest that treatment using activated carbon and flocculation may be more beneficial for wastewater. Therefore, it is recommended that activated carbon is used in wastewater treatment plants to remove organotin compounds.

We also recommend assessing the health impacts associated with tin-stabilized plastic food packaging. This topic was outside the scope of our research, but we think there is potential for tin stabilizers to be ingested after being in contact with food.

Additionally, we recommend further studies on the effects of PVC pipes on aquatic environments. Although toxicity studies on marine environments were referenced, these were mainly to illustrate the general toxicity of organotin compounds. These studies were looking specifically at the effects of marine anti-fouling paints. Organotins are not used in these paints anymore, but there are other routes for organotins to enter marine environments. Therefore, we would recommend assessing the levels of organotin compounds entering these environments to determine if current practices are safe.

Finally, we recommend considering the ways in which other countries have responded to the research currently available on organotin toxicity. As mentioned, most European countries no longer use tin stabilizers for drinking water applications. This is because it became evident that organotins can be toxic when studies on their adverse effects were published. Although North American countries also have access to these studies, tin continues to be the primary PVC stabilizer in North America. It is recommended that other countries' responses to these studies are considered to help ensure that human health is not adversely impacted by tin-stabilized PVC.

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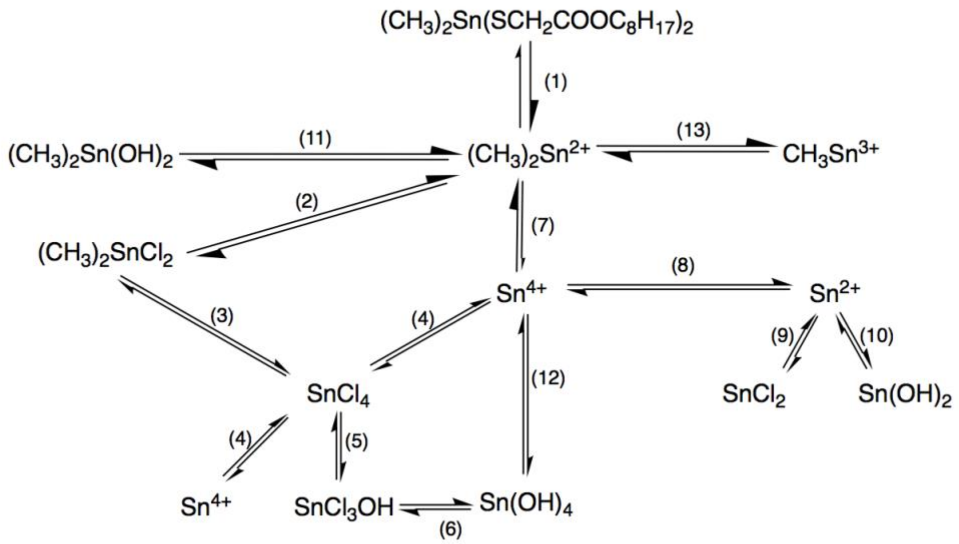
Appendix A: Speciation Diagram and Notes



Corresponding Reactions

1. $(CH_3)_2Sn(SCH_2COOC_8H_{17})_{2\,(S)} \leftrightharpoons (CH_3)_2Sn^{2+}_{(aq)} + 2(SCH_2COOC_8H_{17}^-)_{(S)}$

- Reaction: methyltin mercaptide dissociating into a dimethyltin cation and mercaptide anion.
- Tin in methyltin mercaptide is assumed to be a tin (IV) ion.
  - Hence, dimethyltin is shown to have a +2 formal charge.
  - It is unknown whether dimethyltin commonly exists as an ion, but it was assumed based on information known about the dissociative behaviour of organotin compounds [75].
- The mercaptide ligand is assumed to dissociate from the compound, as organotin compounds have a tendency to undergo dissociation from their anionic ligand in the environment [75].
  - Degradation and the impacts of the anionic ligand in the environment still need to be further explored; however, mercaptides are typically insoluble in water [76].

2. $(CH_3)_2Sn^{2+}_{(aq)} + 2Cl^-_{(aq)} \leftrightharpoons (CH_3)_2SnCl_{2\,(l)}$

- Reaction: dimethyltin ion reacting with chlorine ions in solution to form dimethyltin dichloride.
- Chlorine ions are assumed to be present in the water due to Cl_2 being added to the water during disinfection.

- When chlorine gas is added to water, HCl is formed [77].
- Since HCl is a strong acid, it dissociates into H^+ and Cl^- ions [77].
- Hence, Cl^- ions are expected to be present in the water.

3. $(CH_3)_2SnCl_{2\,(aq)} + Cl_{2\,(g)} \leftrightharpoons SnCl_{4\,(s)} + C_2H_{6\,(g)}$

- Reaction: dimethyltin dichloride reacting with chlorine gas to form tin tetrachloride and ethane.
- It is uncertain whether this reaction would occur in the described environment.
- This reaction was formed by performing a single replacement reaction with dimethyltin dichloride and chlorine gas.

4. $SnCl_{4\,(s)} \leftrightharpoons Sn^{4+}_{(aq)} + 4Cl^-_{(aq)}$

- Reaction: tin tetrachloride dissociating into tin (IV) ions and chlorine ions.
- It is known that tin tetrachloride is soluble in cold water [78].
- The specific Ksp of this reaction is unknown.

5. $SnCl_{4(s)} + H_2O_{(l)} \leftrightharpoons SnCl_3OH_{(s)} + HCl_{(l)}$

- Reaction: tin tetrachloride reacting with water to form tin trichloride hydroxide and hydrochloric acid.
- It is known that tin (IV) chloride forms HCl in hot water [78].
- This reaction is expected to occur when water in distribution systems is heated to a high temperature.

6. $SnCl_3OH_{(s)} + 3H_2O_{(l)} \leftrightharpoons Sn(OH)_{4\,(s)} + 3HCl_{(l)}$

- Reaction: tin (IV) trichlorine hydroxide reacting with water to form tin (IV) hydroxide and hydrochloric acid.
- This reaction was formed by performing a double replacement reaction.

7. $(CH_3)_2Sn^{2+}_{(aq)} \leftrightharpoons 2CH_3^+{}_{(aq)} + Sn^{4+}_{(aq)}$

- Reaction: dimethyltin ion dissociating into a methyl ion and tin (IV) ion.

8. $Sn^{4+}_{(aq)} + H_{2\,(g)} + 2OH^-_{(aq)} \leftrightharpoons Sn^{2+}_{(aq)} + 2H_2O_{(l)}$

- Reaction: redox reaction where tin is reduced and hydrogen is oxidized.
- The two half reactions combine to yield a positive electrochemical potential (0.9787 V), resulting in a thermodynamically favoured redox reaction.

9. $Sn^{2+}_{(aq)} + 2Cl^{-}_{(aq)} \leftrightharpoons SnCl_{2\,(s)}$

- Reaction: tin (II) ion reacting with chlorine ions to form tin (II) chloride.
- $SnCl_2$ is highly soluble; it has a K_{sp} 4.26 x 10^2 in H_2O at 20°C [79].
  - Therefore this reaction is favoured in the reverse direction.
  - Sn^{2+} and Cl^- ions would be present in solution.

10. $Sn^{2+}_{(aq)} + 2OH^{-}_{(aq)} \leftrightharpoons Sn(OH)_{2\,(s)}$

- Reaction: tin (II) ion reacting with hydroxide ions to form tin (II) hydroxide.
- $Sn(OH)_2$ has low solubility; it has a K_{sp} of 1.4×10^{-28} at a temperature of approximately 25°C [80].
  - Therefore $Sn(OH)_2$ is likely to exist as a solid.

11. $(CH_3)_2Sn^{2+}_{(aq)} + 2OH^{-}_{(aq)} \leftrightharpoons (CH_3)_2Sn(OH)_{2\,(aq)}$

- Reaction: dimethyltin ion reacting with hydroxide ions to form dimethyltin hydroxide.

12. $Sn^{4+}_{(aq)} + 4OH^{-}_{(aq)} \leftrightharpoons Sn(OH)_{4\,(s)}$

- Reaction: tin (IV) ion reacting with hydroxide ions to form tin (IV) hydroxide.
- Solubility of tin (IV) hydroxide is unknown.

13. $(CH_3)_2Sn^{2}_{(aq)} \leftrightharpoons CH_3 + (CH_3)_2Sn^{3+}$

- Reaction: Dimethyltin degrading to monomethyltin.
- It is not well understood how frequent this reaction occurs in drinking water pipes; however, monomethyltin is found in drinking water that is conveyed through PVC pipes that contain dimethyltin, so it must occur to some extent [22].