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Caffeine pollution in aquatic environments - treatment and toxicity

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Abstract

Halling-Sørensen *et al.* is credited with introducing the field of emerging pollutants in 1998. The term includes compounds commonly found in the aquatic environment, often stemming from medicine or other products for human consumption. Caffeine is one such compound, and it is found in water bodies all over the world, as a result of human excretion and industrial wastewater. Some wastewater treatment plants effectively remove almost all trace of caffeine pollution, whilst others do not. There is a large variation in treatment rates in different countries and regions. Various methods of detection have been developed, with the goal of making detection cheaper and more availible. Effects from caffeine exposure on aquatic life is a largely underexplored field, but toxicity levels for different species have been found. Behavioural effects for both animals and humans have also been explored.

Contents

1 Introduction

Caffeine (1,3,7-trimethylxanthine) is a psychoactive drug, most commonly consumed via tea, coffee or caffeinated soft drinks. When consumed in small doses, it has a stimulating effect on the nervous system. Larger doses may be fatal, and a potentially lethal dose is considered to be above 10 mg kg^{-1} for an adult human.[1] A person only drinking coffee or tea is unlikely to reach that threshold. Some immediate negative effects of caffeine consumption are known, but the long term effects of chronic exposure to caffeine are not well documented. After consumption of caffeine, less than five percent is excreted unchanged, with the majority having been broken down into mono- or dimethylxanthines.[2] Owing to their similar chemical structure, these xanthines often have similar effects on humans. Paraxanthine (1,7-dimethylxanthine) is the major metabolite of caffeine, and has many of the same stimulating effects, whilst also potentially being less toxic. Xanthines will not be discussed in great detail in this text, but as they are present wherever caffeine is present, they have to be mentioned.

Caffeine is part of a group of compounds called emerging pollutants (EPs). EPs are a wide group of compounds, found in water bodies all over the world. They are released from industry and civilian households, who unknowingly flush them down the sink. This literature review will mainly focus on caffeine, but there will also be comparisons to other EPs.

I wish to focus on mainly two things in this text. What potential effects could caffeine exposure have on humans, animals and plants? Humans have been consuming caffeine for millennia, but this is not the case for animals. As mentioned, negative side effects of caffeine consumption is known for humans. Could some of these side effects be detrimental to how animals live?

Also, what different techniques for removal of caffeine from wastewater exists? Is this actively being researched, or are we content with the current day wastewater treatment techniques? The different methods will be compared, with regards to efficiency, cost and possible environmental impact.

Other aspects of caffeine pollution, such as how widespread it is, will also be discussed. With the field being popularised in the 2000s, a lot of studies around the world have explored caffeine pollution in a lot of different locations. Sadly, some countries and regions are represented more than others, with especially developing countries being underrepresented. Could this change in the future? Traditional detection methods require bulky and expensive equipment, which could explain the lack of studies in developing countries. Could a cheaper and simpler method be developed, to help countries track the level of pollution?

With these questions in mind, I want to present a research question which will be the focal point of the text:

Is caffeine pollution a problem today, and if so, what can be done about it?

2 Theory

This section will introduce theory relevant for the discussion that will follow in a later section. It will be split into different sections, but there might be some overlap between them.

2.1 Background

1,3,7-Trimethylpurine-2,6-dione or 1,3,7-trimethylxanthine, more commonly known as caffeine, is an alkaloid, illustrated in Figure 1. It has the chemical formula $C_8H_{10}N_4O_2$.

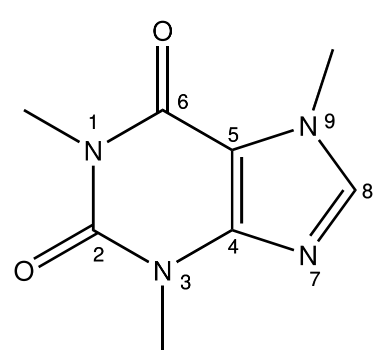

Figure 1: The chemical structure of caffeine.

Caffeine is most commonly consumed through coffee, tea and caffeinated soft drinks. The average consumption of caffeine ranges between 80 - 400 mg per person every day.[3] It is a psychoactive stimulant, giving consumers an energy boost, but as a consequence even small doses affect human sleep negatively.[4] Many also suffer from withdrawal effects of caffeine, such as headaches, fatigue and drowsiness.[5]

Halling-Sørensen *et al.* published a review article about emerging pollutants (EPs) in 1998.[6] It has been credited with focusing the attention of the scientific community to a new field of environmental chemistry. EPs are a loosely defined group of micropollutants in the aquatic environment. Some commonly accepted categories of EPs are pharmaceutical compounds, personal care products, steroid hormones and pesticides.[7]

Caffeine is a small molecule when compared to many other pollutants. It is also a very polar molecule. These properties make caffeine harder to remove from wastewater. The high polarity makes caffeine very mobile in water.[8] Many similar chemicals exist, and in the 1980s the terms persistent polar pollutants and polar persistent organic pollutants were popularised.[9] In recent years, the naming of the terms have moved away from the property polarity, and rather naming them mobile substances.

2.2 Occurrence of caffeine pollution

Caffeine is often found in higher concentrations than many other EPs in wastewater.[7] It has been suggested by different authors as a marker for human or sewage pollution in various water bodies, due to its presence in almost all waters influenced by human emissions.[10,11] The major metabolite, paraxanthine (1,7-dimethylxanthine), has also been suggested as a marker. Paraxanthine concentration levels have not been studied as extensively as caffeine levels, but they are generally found to be equal or higher than caffeine levels.[12]

The sources of caffeine pollution are human excretions, pharmaceutical wastewater and industrial wastewater (e.g. coffee and tea industry). Some researchers point to human excretions being the major source of caffeine pollution.[13] Others argue that industrial wastewater produces more caffeinated wastewater.[14] The coffee industry produces both physical waste and wastewater. The wastewater contains caffeine and other similar chemicals, is acidic, and often not treated before being released into nearby lakes or rivers.[15] These chemicals require oxygen to be broken down biologically, and thus an oxygen deficiency is created in the water, potentially killing nearby animals and plants.[14]

2.3 Effects of caffeine exposure

Caffeine has a lot of well known effects on humans. Both positive effects, such as perceived energy boosts and increased levels of perception and memory, and negative effects, such as nervousness, jitteryness and irritability being common.[16] Some researchers have found that the positive effects of caffeine are merely reversals of the negative withdrawal effects, whilst others have found that caffeine boosts performance also in non-regular caffeine consumers.[17] Caffeine half-life in adult humans range from 3-7 hours, but for newborns the half-life has been found to range from 50 to 100 hours.[16]

Artemia salina is a species of aquatic crustaceans. It is a very resilient species, where eggs can live for years, and because of this it is a common test organism for toxicity in water bodies.[18] Rodriguez-Gil *et al.* estimated a probability curve of an unacceptable risk in different water bodies.[12] In their study, unacceptable risk is considered to be if >5% of the species are susceptible to toxic effects in more than 5% of the cases. They found that unacceptable risk for *Artemia salina* could be expected from exposure to caffeine found in effluent, surface water and estuary water.

Fraker and Smith examined the effects of caffeine exposure for the northern leopard frog (*Rana pipiens*).[19] They found that tadpoles exposed to caffeine were on average smaller than non-exposed tadpoles. Also, while there was no direct impact on the survival rate of the tadpoles, they found that caffeine exposure led to increased activity levels and startle response. They go on to suggest that this could increase susceptibility to predators, as more active tadpoles could be easier to detect for the predators.

2.4 Detection methods

There are multiple ways of detecting caffeine in samples. The most common methods include various separation methods, such as gas chromatography or high-performance liquid chromatography.[20]

They are often coupled with mass spectrometry instruments for detection.[21] These methods have good sensitivities, meaning they can detect low concentrations of caffeine. This is important, as the concentrations in real samples usually are very low. They are not without drawbacks though, as they require bulky and expensive equipment.[22] There is also a need for trained personnel.

Various spectroscopic methods have also been used, with both NMR[23] and FT-IR[24] methods being reported in literature. These methods typically have lower sensitivities when compared to chromatographic methods, and suffer from the same drawbacks, with bulky and expensive equipment needed.

Recently, electrochemical methods have been developed for detection of caffeine. Caffeine is an electroactive molecule, and as it is easily oxidised, it is suitable for electrochemical analysis. Khoo *et al.* developed various graphene platforms for caffeine analysis by voltammetry.[22] They found that graphene derivatives, especially electrochemically reduced graphene oxide (ERGO), provided great performance for detection of caffeine in both prepared samples and real-world samples. ERGO was found to have good selectivity and sensitivity.

The biggest advantage of electroanalytic methods is related to sample preparation. When analysing real-world samples with a chromatographic instrument, extensive sample preparation is needed. The samples need to be extracted and purified carefully. For electroanalytic methods, sample preparation is a lot easier, allowing for faster analysis.

Electrochemical analysis is not without drawbacks, however. Caffeine requires a relatively large positive potential (>1.4V vs. SCE) to achieve reasonable sensitivity.[25] Usage of carbon, graphite or platinum electrodes produced interference from oxidation background currents, which made reproducibility harder. Recent development have shown that graphene and its derivatives have shown good performance for reproducible detection of caffeine.[22]

2.5 Removing caffeine pollution

Figure 2 shows the wastewater treatment rates of different countries in 2018.[26] It is easy to see that the developed countries have higher treatment rates than the less developed countries of the world.

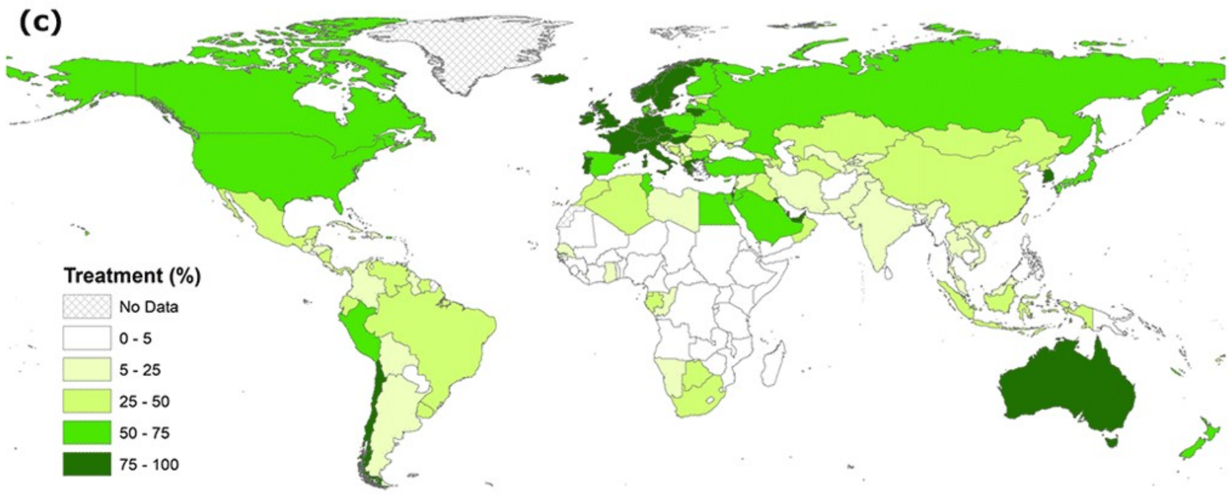

Figure 2: A map of the world showing wastewater treatment rates of different countries in 2018.[26]

The study that created the above map, defined wastewater as any water that had been contaminated as an effect of human activities.

Emerging pollutants (EPs), especially ones that originate from pharmaceutical compounds, are generally found in higher concentration in effluents from hospitals or industry. Verlicchi *et al.* found that the concentration of EPs in hospital effluents was on average 7 times that of the untreated influents from the communal pipes in the same area.[27] Furthermore, they found that 9 of the EPs found in the hospital effluents were detected at concentrations high enough to pose a high risk to the aquatic environment.

Many WWTPs do not remove caffeine from the influent effectively.[28,29] This is especially true for WWTPs that only treat the influent with particle filtration. A German study found that WWTPs that utilise aeration tanks eliminate 99% of caffeine.[13] This is supported by other studies from other countries, reporting similar numbers.[29–31] However, Santos *et al.* reported removal rates between 38 and 86%.[32]

Caffeine removal rates are typically higher than those of other EPs. Zhou *et al.* found removal rates of diclofenac and ketoprofen at 1.2-31.6% and 44.7-71.8% respectively.[29] These figures are consistent with other reports.[30,32] Some other EPs almost get fully removed in WWTPs, whilst other almost pass through unchanged.

There exists multiple techniques for treating wastewater in WWTPs, with both physicochemical and biological methods seeing usage. In recent years, physicochemical methods have been preferred among researchers, for their ability to break down complex compounds fast.[15] Some examples are:

- Zero-valent iron (ZVI) treatment - the iron particulates oxidises and reduces the pollutants in the wastewater, before they precipitate and are remove magnetically. Sadly the ZVI particulates are not easily regenerated, meaning that the process is expensive.[33]
- Photo-Fenton method - utilises a catalytic reaction between ferrous ions and hydrogen peroxide to create a hydroxyl radical, which is a powerful oxidant.[34] However, it requires hydrogen peroxide, which is not regenerated in the reaction. The reaction is most effective with a pH in the solution of around 3, which is too acidic to be released from the WWTP, and thus requires further treatment.
- Electro-oxidation - utilises electrolysis to oxidise the pollutants. It has two ways to this, either directly on the surface of the electrode, or indirectly, by creating reactive radicals, such as hydroxyls or chlorine radicals, which in turn oxidise the pollutants.[35] A downside here is that the method uses a lot of electric energy.[36]
- Treatment with ion exchangers - ion exhange polymers with basic and/or acidic functional groups change the charge of the pollutants, and then create physical bonds to them, keeping them from leaving the WWTP. This method removes all ionic and ionizable species from a solution. It does however require filtration beforehand, and the method has not been explored widely for coffee wastewater treatment.[15]

The most common method today is the one mentioned above, namely aerobic/anaerobic digestion. Here aeration tanks where bacteria is responsible for degradation of the pollutants are used to treat the wastewater.[15] The method is often combined with a physical filtration beforehand, to remove any solids suspended in the wastewater. This method is time-consuming, and the volume and strength of the effluent is not necessarily consistent every time. This means that the effluent usually requires further treatment, to ensure that it is clean enough for release into water bodies.

3 Discussion

At present, the risk of humans experiencing negative effects from caffeine pollution is considered low.[12] This is not unexpected, as humans have been consuming caffeine for millennia through coffee and tea based drinks. As mentioned in Chapter 2.1, caffeine has known negative side effects, but it is rarely deadly, with only a few cases reported in literature. There are however, a lack of studies discussing the long term effects of caffeine exposure affecting humans. Children and infants, especially, could be susceptible, as caffeine effects vary with body weight and caffeine has a longer half-life for infants. This potentially means that smaller doses could have longer effects on children.

Adverse effects on animals have also been reported. Both behavioural effects, such as reducing investigatory behaviour for mice,[37] and potentially toxic effects have been studied. Interestingly, positive effects have also been reported. Cunha found that caffeine had no effect on the memory of unstressed mice.[38] However, stressed mice injected with caffeine showed better memory than stressed mice with no caffeine exposure. This could indicate that caffeine acts as a normaliser; helping decrease negative effects of stress, but not improving upon normal cognitive function.

Some researchers have found similar effects in humans, with the withdrawals effects of caffeine being cancelled by further caffeine consumption. This could potentially lead to a caffeine addiction, which again could lead to poor sleep and increased levels of fatigue. Other researchers have found caffeine to boost perceived energy and memory in both regular caffeine consumers, who could experience withdrawal symptoms, and also in non-regular caffeine consumers, with no withdrawal symptoms.

In raw wastewater, where the caffeine concentrations are typically highest, the concentration levels are generally not high enough to pose a risk for acute poisoning for animals nor humans. However, the thresholds for potentially toxic caffeine concentration levels are lower for chronic exposure.

Other EPs are more often found with potentially toxic concentration levels in WWTPs. When Verlicchi *et al.* studied hospital wastewater, they found four different antibiotics at concentrations where they could pose a risk to aquatic life. They go on to say that hospital wastewater, which typically is high in medicinal EPs, is usually treated at the same facilities as normal civilian wastewater. They argue that hospital effluent should be pre-treated before being released into the communal pipes, because the medicinal EPs are typically not removed by traditional WWTPs. While this certainly would help, it would be expensive. An alternative would be to increase focus on safe handling of medicinal waste, instead of flushing them into the general wastewater pipes.

In general, from current research, it is hard to conclude on whether caffeine pollution is likely to affect humans or animals in the long term. There is a large amount of research papers documenting both positive and negative effects of caffeine, but these are usually discussing levels of caffeine concentration that are unlikely to occur from only consuming caffeine-polluted water, especially at the levels of caffeine concentration found today. Further studies to quantify the thresholds of toxicity, especially for humans, is needed.

Some studies have compared the presence of caffeine in recent times with data from over 20 years ago.[39] They usually show a lesser concentration now compared to the previous studies. This is likely due to the increased focus on treating wastewater, instead of releasing raw wastewater into the ocean. This is backed up by the fact that caffeine has been found to have a half-life of up to 100 days in seawater samples.[40] Caffeine consumption and subsequent release into water bodies has not decreased over the last 20 years, and thus the caffeine concentration is unlikely to decrease by itself.

The majority of the studies looking into caffeine concentration stem from developed countries. The lack of WWTPs in developing countries could lead to a higher concentration of caffeine being released into the ocean. The lack of studies make comparing less accurate, as the data does not necessarily accurately represent the actual levels of caffeine in different regions. With that uncertainty in mind; caffeine concentration levels in surface waters have been on average reported to be between one and two orders of magnitude larger in Africa and South America when compared to Europe and North America.[12] When looking at the map in Figure 2, a clear trend is that the latter regions treat over 50% of the produced wastewater, whilst the former regions (with some exceptions) treat under 25%.

There is also the possibility that the higher levels of caffeine concentration is due to the coffee and tea industry producing waste. Coffee production produces caffeine-containing waste, due to the way coffee beans are produced. Similarly to the hospital wastewater, the wastewater produced by the coffee industry is typically not treated before being released. Additionally, a not insignificant amount is released into nature, instead of being released to communal WWTPs.[15]

The coffee bean grows inside a berry, which is discarded (often in nature or lakes) before being shipped around the world. From an economical perspective this makes sense, as less weight equals cheaper shipping, but the caffeine-containing pulp does pollute the nearby nature. Additionally, washing coffee beans requires a lot of water, which when exposed to coffee beans become caffeinated wastewater. As mentioned, both the pulp and the caffeinated wastewater is often released into the wild, and not handled properly. This could explain the higher levels of caffeine found in Africa and South America, as they are both major hubs for coffee production.

Traditional WWTPs do not specifically focus on removing caffeine or other EPs. Traditional in this context denotes either filtration based WWTPs or aeration tank-based WWTPs. Caffeine, along with other EPs, are pollutants that have not been the focus of WWTPs for a very long time, with the field only really coming into focus in the early 2000s. Much of today's treatment infrastructure is older than this, and there is also a big possibility that even more recent infrastructure focus more on well known pollutants, such as metals, bacteria, nitrates (NO_3^-) and ammonia (NH_4^+). These pollutants have well documented negative effects, and regulations for their treatment have been in place for decades.

Despite this lack of focus of EPs, some studies report caffeine removal rates that are well over 90%.[13,29–31] These studies all come from cities where WWTPs utilise aeration tanks, where bacteria are responsible for breaking down the pollutants. Sadly, no studies looking at real world efficiency of the alternative physicochemical methods could be found.

Other studies have reported lower numbers. Santos *et al.* compared the effluent and influent of four different WWTPs in the city of Seville, Spain.[32] They found that removal rates for all of the EPs they looked at, including caffeine, differed a lot from one WWTP to another. For caffeine, the removal rates varied from 38% to 86%. The four WWTPs studied all used similar treatment techniques, namely aeration tanks.

The difference in removal rate highlights a downside of biological aeration treatment. The lack of consistency means that the quality and cleanliness of the effluent cannot be guaranteed, meaning that further treatment would be needed. Santos *et al.* did not present a conclusive answer as to why some WWTPs performed better than others. They did however predict a connection to the general water quality. When comparing the WWTP that had the highest caffeine removal rate to the WWTP that had the lowest, one major difference between them was the estimated number of inhabitants served. The WWTP that performed worst, served approximately three times as many inhabitants. Interestingly though, the two middle-performing WWTPs both served less inhabitants than the best performing WWTP. As there is generally a lack of studies discussing the causes of varying effectiveness of the WWTPs, it is hard to conclude on why this is the case. It is also interesting how all four of the WWTPs studied in Seville report lower numbers than those in other cities. Further comparisons between the influent wastewater could give insight into what exactly produces the inconsistent results. Some factors that potentially could affect the effectiveness of the aeration-based WWTPs are the water quality of the influent (e.g. amounts of pollution and oxygen present), the time spent in the treatment facility, the quality of the pre-treatment (i.e. filtration in most cases). The bacterial culture also varies between facilities, and it is possible that some cultures break down caffeine and other pollutants more efficiently.

The different techniques for treatment of wastewater mentioned in Section 2.5 all have their advantages and disadvantages. They all generally produce more consistent removal results than the aeration tanks. One major disadvantage of all the new methods for treating wastewater is cost, as installing anything new on a large scale is expensive.

Additionally, both the zero-valent iron treatment, and the Photo-Fenton require replacement of the materials used. They are both very efficient at removing caffeine and similar pollutants from wastewater. However, due to them not being regenerable, the long-term cost and potential environmental consequences probably make them not viable for large-scale WWTP usage.

Usage of electro-oxidation methods might circumvent these issues. However, it has a high cost of entry, making it a costly investment for new WWTPs. There is also the need for electricity, which needs to be optimised and lowered before electro-oxidation is a viable method for removal of pollutants.

Some scientists have suggested usage of ion exchangers for treating EPs present in wastewater. They suggest that a lot of EPs, including caffeine, are easily ionised, and as such, can be removed (more precisely exchanged out) with ion exchanger treatment. Similar methods are currently seeing usage to "soften" water, so it is not unlikely that it could work very well for caffeine removal. The method has not been studied for caffeinated wastewater treatment, so the actual efficiency is not known.

Usage of aeration tanks for aerobic and aerobic bacterial digestion is the most popular treatment method today, and that is likely to continue. It is a relatively cheap method to implement, and it is easy to scale up. However, as mentioned above, the method produces inconsistent results. In addition, the process is time-consuming. The bacterial environment requires time to adapt to the environment in the wastewater.

Generally speaking, the focus should be on getting the water treatment percentage up on a worldwide basis. That means installing more WWTPs and generally improving wastewater infrastructure. If that is to happen, the major factor is cost, and thus aeration tanks are the best option. With further focus on how to increase removal of caffeine and other EPs, it is possible to imagine traditional WWTPs eliminating caffeine at rates close to 100%. If that were to be the case, the next task would be to ensure an increased amount of WWTPs in developing countries, to raise their water treatment percentage.

4 Conclusion

Today, there is little doubt that caffeine pollution is present in water bodies all over the world. It is well documented, and even lakes that are close to isolated have been shown to contain some caffeine. The cause of this pollution is also well known, with sources being human excretion, and wastewater from industries, especially tea, coffee and the medical industry. While industrial wastewater typically has a higher concentration of caffeine, it is currently not known whether civilian or industrial wastewater is the biggest overall contributor to caffeine release.

There is a lack of knowledge around the effects of caffeine pollution. The negative effects of normal human caffeine consumption from coffee and tea are well documented, with lack of sleep and fatigue being the most common. Exposure from drinking water is very low, but in most cases not zero.

This leads to humans being chronically exposed. The effects of this have not been explored, with most studies looking at higher concentrations. As children are more likely to experience negative effects from caffeine, they could possibly be affected more by chronic caffeine exposure. Further research is needed before any conclusions can be drawn.

Animals could also be at risk. The majority of studies examining effects of caffeine exposure on animals, study concentrations of caffeine that are some orders of magnitude higher than what is present in water bodies today. This means that while both positive and negative effects from these studies have been reported, they are not necessarily representative of the danger that animals could face in the real world.

Various analysis methods have been used for determining caffeine concentration levels in water bodies. At present, various chromatographic methods, especially GC and HPLC, sees most usage. They exhibit good sensitivity, but require expensive equipment. Khoo *et al.* argued for the development of electrochemical analysis for caffeine determination, as they found them to have good selectivity and sensitivity for caffeine analysis. They argue that it could be a cheaper method of analysis, thus making it more accessible. This could help researchers get a clearer picture of caffeine pollution worldwide.

Aeration tanks are the most common treatment method being used today. They are often paired with some filtration method, to remove solids suspended in the wastewater. The method was not developed with caffeine or EPs in mind, and this is shown with research showing varying effectiveness. However, the majority of the studies conducted reported removal rates in the high nineties, indicating that aeration tanks are generally effective at removing caffeine from wastewater.

The issue is that the general water treatment levels are very low in some parts of the world, with many countries treating less than 50% of their produced wastewater. An increase in WWTPs are needed, and some researchers point to this as an excellent opportunity to install new technology for water treatment. Others argue against this, proposing that improvement to bacterial treatment with aeration tanks is more important. There has also been proposals to install treatment facilities on site, meaning that industrial wastewater is cleaned at their facility, before entering communal WWTPs. This would probably ensure good treatment of wastewater, but the idea might not be economically viable.

To conclude, caffeine pollution is not a major issue worldwide. The general consensus is that concentration levels are trending downwards, and additionally, no major health issues have been found for animals nor humans. Despite this, it is important to keep improving wastewater treatment worldwide, to ensure that caffeine levels stay low.

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