MOLEAER
ADVANCING NANOBUBBLE TECHNOLOGY

SURFACTANTS IN WASTEWATER:

UNINTENDED CONSEQUENCES OF WATER CONSERVATION AND THE PANDEMIC

CONTENTS

SURFACTANTS IN WASTEWATER: A GROWING CHALLENGE

Regardless of industrial or municipal applications, these are the most common observed wastewater challenges:

- Rising energy and chemical costs
- Treatment capacity constraints – inability to meet effluent requirements
- Fats, Oil, Grease (FOG); scum and odor issues
- Frequent process upsets, toxicity events and inconsistent performance
- Bulking sludge, filamentous bacteria problems and poor sludge settling.

These challenges cause facilities to perform outside their design conditions, making them unreliable. The root cause for these challenges is the increased presence of **surfactants**, which interfere with solids separation, biological processes, and oxygen transfer—all critical factors in effective water treatment.

Figure 1: Surfactants are commonly used in liquid soaps and detergents.

"**Surface-active-agents**," also known as surfactants or *tensides* are amphiphilic compounds, made up of a long hydrocarbon chain (the hydrophobic or water-hating region) and a polar head group (the hydrophilic or water-loving region). The hydrocarbon chain is attracted to other hydrocarbons, while the polar head group is attracted to water. This allows surfactants to form interfaces between water and other liquids, or between water and solids. They have the specific property of being able to reduce surface tension and interfacial tension, which makes them useful for a variety of applications including:

- Soaps and detergents (sodium lauryl sulfate (SLS) is a common surfactant ingredient)
- Surface cleaners, degreasers, emulsifiers, wetting and foaming agents
- Quaternary ammonium compounds (QACs or quats) – e.g., benzalkonium chlorides (BACs), commonly used in consumer and industrial products including disinfectants and as an anti-microbial preservative for pharmaceutical products.

How Surfactants Function as Soaps & Detergents

The mystery of soap's ability to clean oil and grease, yet not water, lies in the science of surfactants. Surfactants, like soaps and detergents, share a surprising similarity with the very substances they remove – fats, oils, and grease (FOG). Both have a unique structure that enables them to repel and attract water.

Imagine both surfactants and FOG as mini magnets with two poles. The “water-loving” pole attracts water, while the “water-hating” pole attracts other water-hating compounds like oil and grease. This dual attraction allows surfactants to encase FOG molecules, like a protective shell.

When soap is applied, these soapy shells surround the oil molecules, effectively pulling them away from the surface they cling to. This process allows the water to wash away the now-detached oil and grease, leaving the surface clean. In essence, soap’s cleaning power lies in its ability to “out-attract” oil and grease from surfaces, effectively dissolving them and allowing water to carry them away.

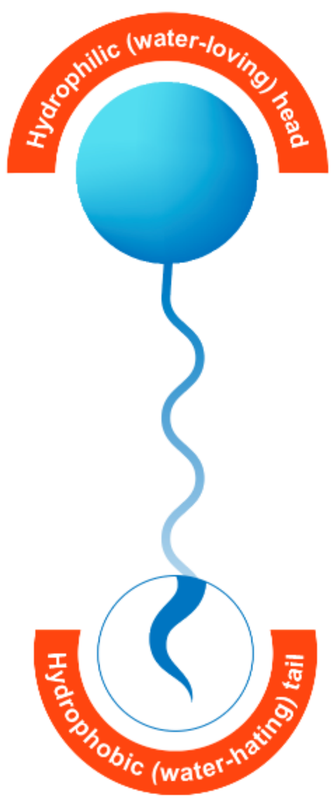

Figure 2: Surfactants are amphiphilic compounds with a hydrophobic tail and hydrophilic head.

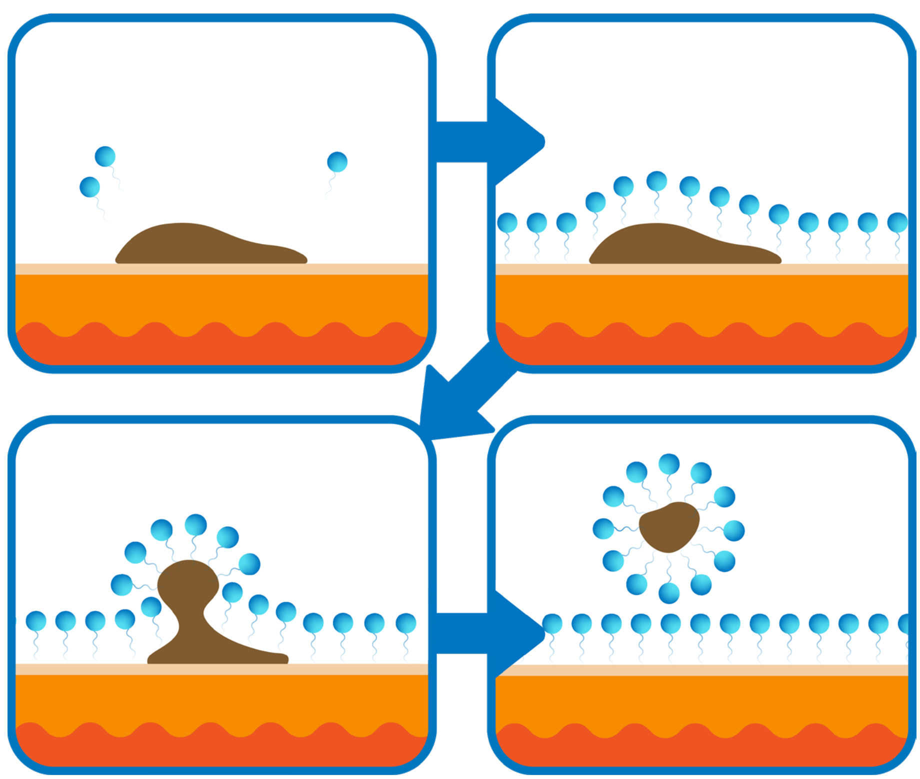

Figure 3: Surfactants in soaps help remove dirt from surfaces by coating, detaching and allowing water to wash it away.

Trends in Water Conservation and Surfactant Usage

Global domestic water usage has been steadily declining over the past few decades. This has been due to various conservation efforts and an effort to make all household appliances like dishwashers, washing machines, showers, and toilets more efficient.

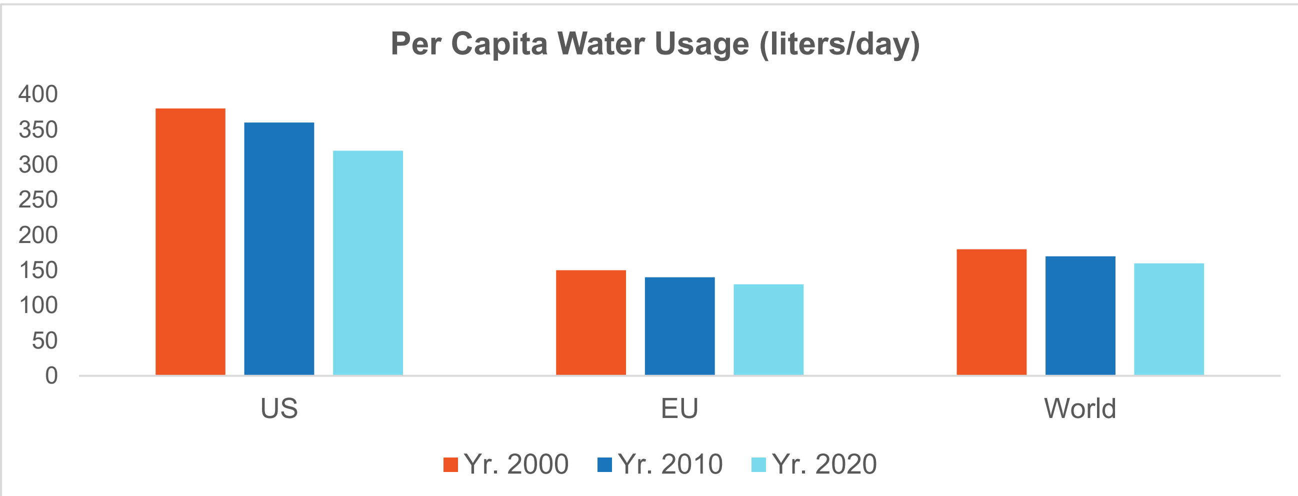

Figure 4: Per capita daily water usage in liters for the United States, Europe and the World from 2000 to 2020.

While water usage globally has been steadily declining, the usage of cleaning chemicals—both in potency and quantity—has been steadily increasing. The Covid-19 pandemic accelerated the use of cleaning chemicals across the world. The increasing concentrations of surfactants are an unintended consequence of the global efforts to reduce our water footprint.

It's the increased concentration of surfactants that have adverse effects in wastewater treatment and result in commonly observed wastewater challenges. According to Metcalf and Eddy in their 2007 paper,[1] raw municipal wastewater contained around 4-10 mg/L of surfactants that year. In water-stressed areas, surfactant concentrations greater than 20 mg/L have been observed in recent years.

Industrial and other users of water have been tracking a similar path. Globally, industries are looking for ways to improve sustainable water use, including conservation efforts due to climate change, population growth and rising costs *(Reig et al., 2013).* This has enabled industries to decrease the water-to-product ratio *(BIER, 2013).* Though these are positive trends, the more concentrated influent waste has negative outcomes in existing wastewater treatment systems that tend to underperform.

[1] Metcalf and Eddy publication.

What are the Negative Impacts of Surfactants on Wastewater Treatment Processes?

While surfactants help to clean, they can also stabilize emulsions of oil and water, making them more difficult to break down. This can lead to a fatberg formation,[2] a hard mass of waste matter that collects and clogs sewer systems. Concentrations exceeding 15 mg/L of SLS reduce oxygen transfer efficiency by 50%, compared to clean water *(Rosso, 2018).*

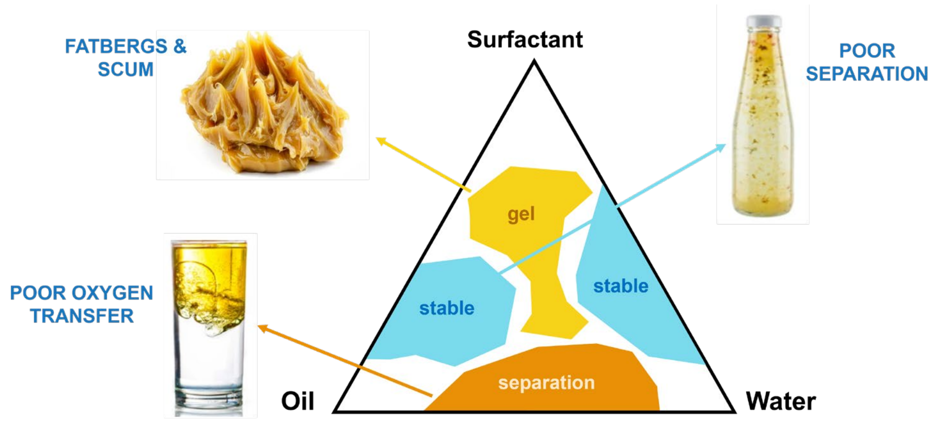

Figure 5: Concentrations of surfactants, oils and water play a critical role in the development of stable emulsions, scum and fatbergs.

Additionally, total inhibition of nitrification can occur at levels as low as 1.5 mg/l of BACs, an industrial cleaning quat, on unacclimated sludge *(Conidi et al., 2019).* Nitrification is the biological process where ammonia is converted into nitrate by bacteria. This process reduces ammonia toxicity and helps wastewater treatment plants and lagoons comply with discharge regulations. When nitrification is inhibited, it means that the bacteria is not functioning properly, and the conversion has been slowed or stopped. Inhibition can lead to increased ammonia, reduced treatment efficiency and odor problems.

The Physical Impacts of Surfactants in Wastewater

- Creation of stable emulsions that hinder efficient separation/clarification
- Coating of biomass, suffocating the fixed-film and suspended growth systems
- Coating of water surface, decreasing the surface oxygen transfer
- Reducing aeration efficiency by obstructing oxygen transfer through the bubble
- The smaller the bubbles, the longer their residence time, allowing for more surfactant accumulation and therefore more efficiency losses
- Refraction of light and reduction of beneficial algae growth in facultative lagoons, which promotes septic conditions that cause odors and ammonia release
- Increasing the turbidity, which decreases UV transmission and impacts tertiary and reuse treatments

In addition to all the above effects on aerobic systems, surfactants have adverse effects on anaerobic systems as well; specifically, 38% to 96% of influent QACs sorb to biosolids. QACs do not biodegrade under anaerobic conditions, instead accumulating in the digesters, causing foaming and inhibiting methanogenesis, the process of making methane from anaerobic digesters (Hora et al., 2020).

[2] Learn more about fatbergs.

How are Surfactants Measured?

While surfactants are present in most wastewater streams, they are extremely difficult and expensive to measure in the field or a lab. However, one can measure and observe:

- Plant/blower power draw – increased energy use
- Process upsets and toxicity affecting dissolved oxygen
- Declining effluent water quality
- Increased need for chemicals
- Excessive odors, foam and/or scum

What can be Done to Reduce the Detrimental Effects of Surfactants on Wastewater?

In low concentrations, surfactants can be treated using traditional aerobic biological systems. However, in most wastewater facilities, these concentrations exceed design limits, causing many of the issues highlighted earlier.

Due to their tendency to coat surfaces, surfactants will ultimately end up in anaerobic digesters. However, they are resistant to biodegradation in anaerobic environments and instead accumulate in the digesters. This accumulation leads to foaming issues and inhibits methanogenesis, both of which negatively impact digesters' effectiveness.

Common practices for managing these inhibitory compounds include:

- **Increasing DO, since most surfactants degrade aerobically**. However, this may cause DO carryover to anoxic zones, in addition to increased energy usage and aeration costs.
- **The use of chemical sequestrants that bind to surfactants and stop them from sorbing to bubbles and biomass.** However, these accumulate in anaerobic digesters, causing foaming and inhibition. In addition to increased costs, there are regional regulations prohibiting the usage of these chemicals.
- **Increasing sludge retention times (biomass) to recover from inhibitory slug loads.** This increases aeration energy usage and costs while decreasing the activated sludge treatment capacity.

Nanobubbles, when deployed in the right locations, have unique characteristics that reduce the inhibition of surfactants. These charged nanoparticles improve separation processes and enhance the treatment ability of wastewater plants, without any drawbacks.

NANOBUBBLE TECHNOLOGY: A ROBUST, CHEMICAL-FREE SOLUTION

Unique due to their size, nanobubbles deliver significant value in water treatment and the environment. In wastewater treatment, chemical-free nanobubbles work like clean chemistry to enhance separation processes and intensify biological processes.

Enhance Separation Processes:
Due to their surface properties and stability, nanobubbles act like natural coagulants, improving separation processes, especially in waste streams with high levels of FOG.

Intensify Biological Processes:

- **Protect Biological Processes:** Nanobubbles accumulate hydrophobic materials such as FOG and surfactants on their surface, shielding downstream biological processes from the inefficiency and process upsets caused by these compounds.
- **Increase Biological Treatment Efficiency:** Nanobubbles improve biological treatment efficiency, including nitrification and nitrifier growth rates, enabling facilities to optimize their process for desired outcomes (e.g., more treatment capacity, better effluent water quality, improved energy efficiency, more resilience, reliability and/or faster recovery from process upsets).

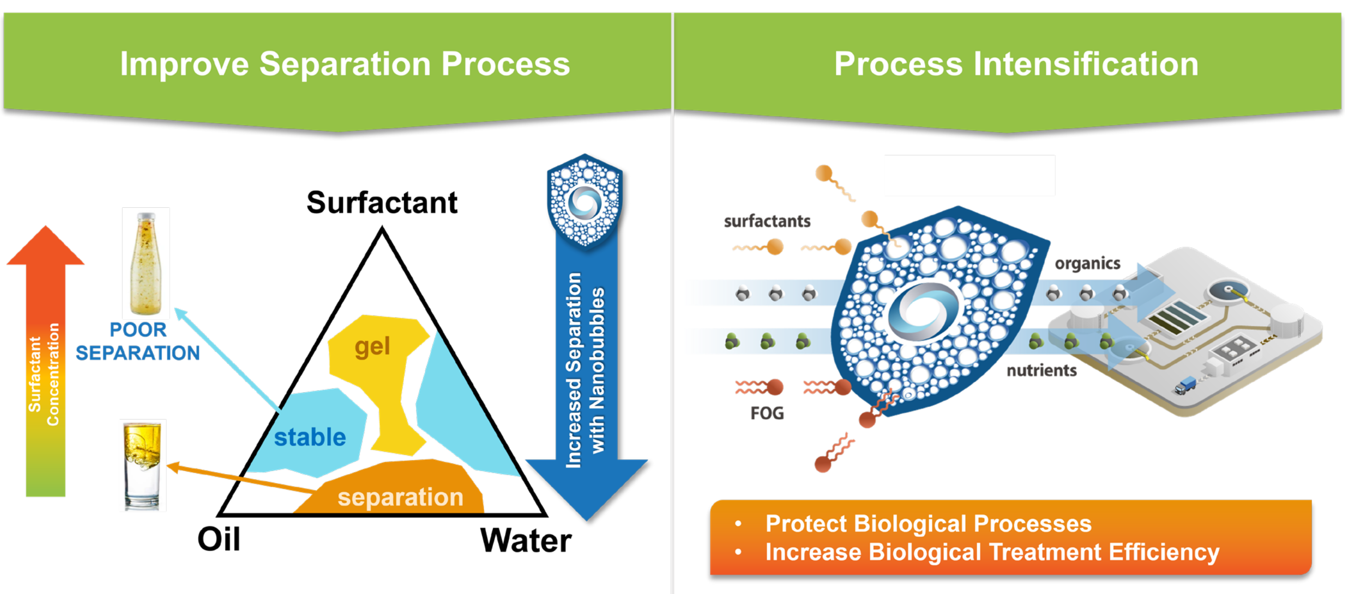

Figure 6: Benefits of nanobubbles in wastewater treatment.

Using these properties, nanobubbles help wastewater plants combat surfactant inhibition, reduce emulsification and convert slowly biodegradable chemical oxygen demand (COD) to readily biodegradable COD, resulting in process intensification.

- **Size:** The nanobubble is defined as a bubble that is <200 nanometers in diameter. Compared to a typical 1 mm bubble, 100-nanometer bubbles provide 10,000 times more interfacial surface area within the same volume for adsorbing inhibitory compounds.
- **Charged:** Nanobubbles have a strong negative surface charge that prevents them from coalescing. This allows them to spread throughout the water body.
- **Stable:** Nanobubbles are neutrally buoyant, meaning they don't rise to the surface and pop, as larger bubbles do. Instead, they remain suspended in water, allowing time for reactions to happen.
- **Hydrophobic:** Nanobubbles are hydrophobic. As such, they attract other hydrophobic materials like surfactants, cleaning chemicals and FOG, thus disabling their inhibitory effects on wastewater treatment.

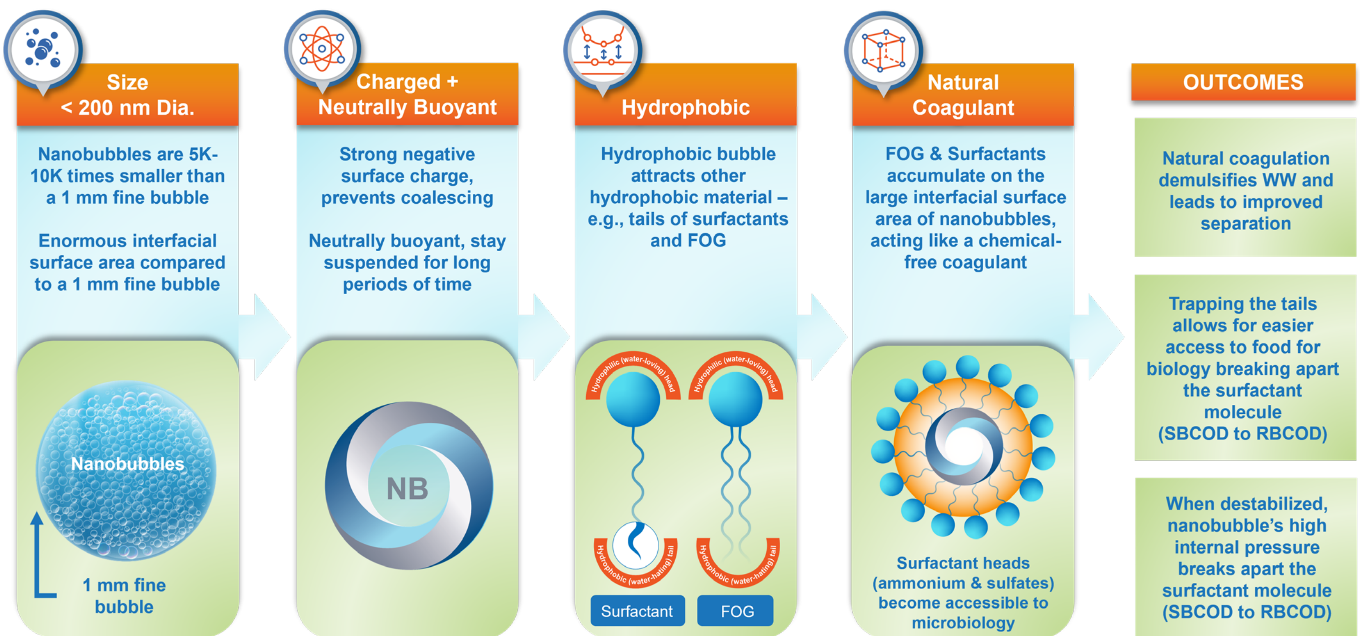

Figure 7: How surfactants and other compounds are removed from wastewater with nanobubbles.

SUMMARY

The escalating presence of surfactants in wastewater presents a formidable challenge to industrial and municipal treatment facilities worldwide. These amphiphilic compounds, while effective in cleaning applications, disrupt critical processes in water treatment, leading to a cascade of issues including reduced treatment efficiency, increased energy consumption, and environmental hazards such as fatberg formation and foaming. Despite global efforts to reduce water usage, the use of cleaning chemicals, including surfactants, continues to rise, exacerbating the problem.

Traditional methods for managing surfactant-contaminated wastewater, such as increasing aeration or using chemical sequestrants, come with their own set of drawbacks and limitations. However, emerging technologies such as nanobubbles offer a robust, chemical-free solution to mitigate the adverse effects of surfactants. By leveraging the unique properties of nanobubbles, wastewater treatment plants can effectively reduce surfactant inhibition and enhance treatment efficiency, without the drawbacks associated with traditional methods.

Incorporating nanobubble technology into wastewater treatment processes represents a significant step forward in addressing modern treatment challenges, ultimately leading to more reliable and sustainable water treatment practices. As we continue to innovate and adapt to the evolving landscape of wastewater management, it is crucial to embrace technologies that offer both effective solutions and environmental benefits.

Moleaer Inc. | Hawthorne, CA, USA | Almería, Spain | info@moleaer.com

REFERENCES

Arora, J., et al. (2022). Surfactant pollution, an emerging threat to ecosystem: Approaches for effective bacterial degradation. *Journal of Applied Microbiology*, 133(3), 1229-1244. https://ami-journals.onlinelibrary.wiley.com/doi/full/10.1111/jam.15631

BIER. (2013). Bier Issues Results of 2012 Water Use Benchmarking Study. https://www.bieroundtable.com/news/bier-issues-results-of-2012-water-use-benchmarking-study/

Conidi, D., et al. (2019). Modeling quaternary ammonium compound inhibition of biological nutrient removal activated sludge. *Water Science & Technology*, 79(1), 41-50. https://iwaponline.com/wst/article-abstract/79/1/41/64467/Modeling-quaternary-ammonium-compound-inhibition

Ellsberry-Cowan, C., et al. (2014). Environmental Safety of the Use of Major Surfactant Classes in North America. *Environmental Science Technology*, 44(17), 1893-1993. https://pubmed.ncbi.nlm.nih.gov/25170243/

Hora, P.I., et al. (2020). Increased use of quaternary ammonium compounds during the SARS-CoV-2 pandemic and beyond: consideration of environmental implications. *Environmental Science Technology*, 7(9), 622-631. https://pubs.acs.org/doi/10.1021/acs.estlett.0c00437

Mackie, A. *Treatment Plant Q&A: Can QACs Disable Wastewater Treatment?* CWEA. https://www.cwea.org/news/treatment-plant-qa-can-qacs-disable-your-process/

Metcalf & Eddy, Inc., et al. (2007). *Water Reuse: Issues, Technologies, and Applications*. 1st ed. New York: McGraw-Hill. https://www.accessengineeringlibrary.com/content/book/9780071459273

Reig, P., et al. (2013). Water Stress by Country. https://www.wri.org/data/water-stress-country

Rosso, D. (2018). *Aeration, Mixing, and Energy: Bubbles and Sparks*. IWA Publishing. https://doi.org/10.2166/9781780407845