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Perspective

# Environmental Exploration of Ultra-Dense Nanobubbles: Rethinking Sustainability

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**Abstract:** Nanobubbles are nanoscopic gaseous domains than can exist on solid surfaces or in bulk liquids. They have attracted significant attention in the last decade due to their long-time (meta)stability and ready potential for real-world applications, especially in environmental engineering and more sustainable ecosystems, water treatment, irrigation, and crop growth. After reviewing important nano-bubble science and activity, with some of the latest promising results in agriculture, we point out important directions in applications of nano-bubble phenomena for boosting sustainability, with viewpoints on how to revolutionise best-practice environmental and green sustainability, taking into account economic drivers and impacts. More specifically, it is pointed out how nanobubbles may be used as delivery vehicles, or “nano-carriers”, for nutrients or other agents to specific targets in a variety of ecosystems of environmental relevance, and how core this is to realising a vision of ultra-dense NBs in shaping a positive and lasting impact on ecosystems and our natural environment.

**Keywords:** nanobubbles; delivery; water; agriculture; ecosystems

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## 1. Introduction

Nanobubbles (NBs) are nanoscopic gaseous domains than can exist on solid surfaces or in bulk liquids. They have attracted significant attention in the last decade [1–3] due to their long-time (meta)stability and high potential for real-world applications. Amongst these applications, NBs can be applied towards nanoscopic cleaning [4], control of boundary slip in microfluidics [5], wastewater treatment [6], hetero-coagulation [7], and medical applications [8]. Although surface NBs have been formed and observed using various experimental methods, bulk-liquid NBs have been much less investigated. It has been conjectured that the long-lived presence of nanobubbles is due to negative-charge build-up at the bubble/liquid interface, with the surface having a strong electron affinity [9]: an opposing Coulombic force to surface tension slows the bubbles’ dissipation.

The thermodynamic metastability of nanobubbles for many months or longer lies in stark contrast to micron-sized bubbles as a puzzling conundrum [10–12]. In addition, NBs’ other unique physical and mechanical characteristics, such as dramatically reduced buoyancy, extremely high surface area/volume ratio, large zeta potentials, generation of free radicals, and slow-rising velocity, are very poorly understood [11–13]. Several commercial applications of nanobubbles have been identified to date, such as improved performance of fine-particle flotation [14–18] and superior mass transfer of gases in separation and reaction engineering [16,19,20]. Nanobubbles have shown potential for use in water treatment [21,22], in sterilisation by applying ozone gas [23–25], and in accelerating the metabolism in shellfish and vegetables [26–28]. There are considerable potentials of NBs for the soil remediation polluted by organic chemicals in combination with bioremediation [29,30]. In the medical field, the unique properties of nanobubbles are harnessed as a contrast agent for ultrasonographic diagnostic scanning as well as drug and gene delivery [31,32], and also as an oxygen-delivery source for wounds [33,34].

In terms of soil remediation in the general environment, particularly in water-stressed regions and for grassland management and cultivations, Hashim et al. in 2012 and Li et al.

in 2013 discussed cogently how NBs may be used to transfer additional nitrogen, in the form of NBs [29,30], into the soil itself, and for such soil-based bacteria to then be able to fix this into a more bio-available form. Importantly, this has a positive and healthy effect on soil behaviour and dynamics.

Nanobubbles, as the gas-containing exponent of the more general case in what one might call usefully the nano-phase (encompassing both bubbles and droplets at the nanoscale), can be categorised broadly into two: (i) surface and (ii) bulk nanobubbles, depending on their nucleation media. Surface nanobubbles are present at most aqueous surfaces where they persist, often perhaps for weeks [1], with many more investigations made into surface nanobubbles than their bulk counterparts [35]. Bulk nanobubbles are present in most aqueous solutions, possibly being continually created by agitation and cosmic radiation [1,36]. Their concentration increases upon stirring and reduces upon filtration or degassing [37]. In more detail, the contact angles of surface NBs are relatively small, usually about 5 to around 20°, and they tend to accumulate at hydrophobic surfaces and at hydrophilic substrates [1,35]. With changing dissolved-gas levels in the liquid, such surface NBs either grow or diminish in size [1,35]. When dissolved-gas levels are reduced, surface NBs tend to become smaller, albeit retaining their metastability, in stark contrast to any thermodynamic predictions. In contrast, bulk NBs typically have diameters of 50–200 nm, and their size can respond to ions and additives. There is much industrial and ecological interest in the presence of bulk NBs, in that their occasional long life and stability, depending on their method of generation and bulk-liquid conditions, often exceeds the residence time of many processes such as aeration cycles in activated-sludge tanks for wastewater treatment and recirculation-aeration systems, or more broadly, for water-body aeration [1,35,36].

A bibliometrics literature survey for scientific articles on nanobubble applications and generation techniques is presented in Figure 1; it can be concluded that interest lies mostly in investigating disparate biological- and medicine-applications, whilst less than a third of studies have focused on different techniques of nano-phase generation *per se* and underlying elucidation and characterisation.

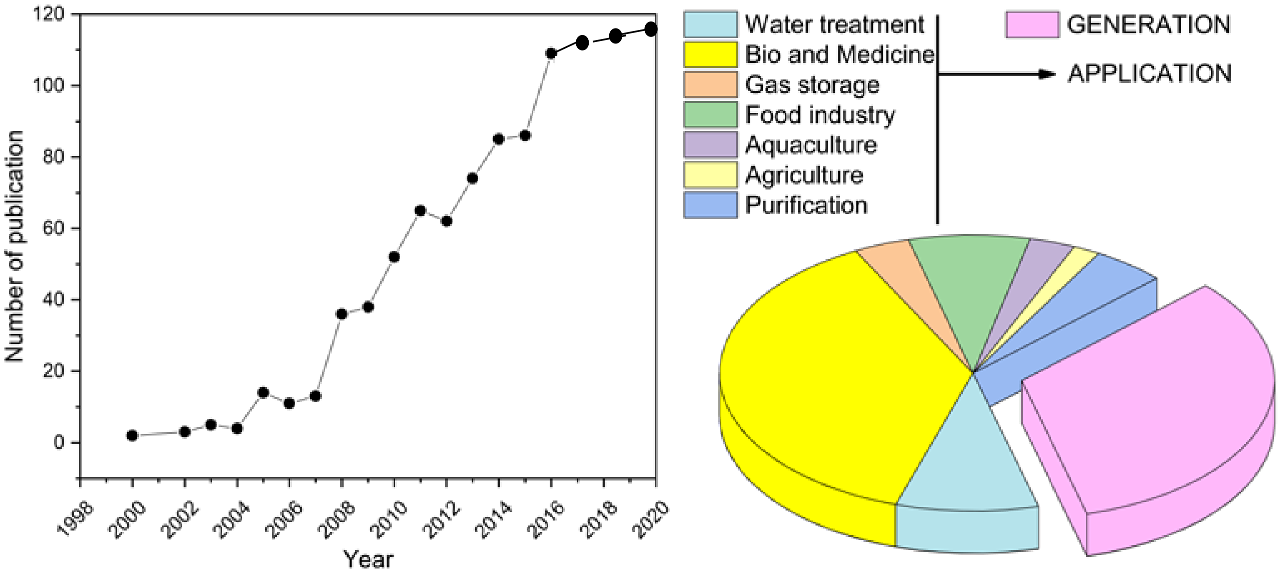

**Figure 1.** A 20-year literature search on nanobubble-related publications; various keywords listed above. Image credit: adapted from one supplied by M.R. Ghaani.

## 2. Microscopic Fundamentals

Generally, as with larger bubbles, nanobubbles have a negative zeta potential (≈−25 to −40 mV) in neutral solutions, as proven by electrophoretic light scattering. They are under excess pressure, as surface tension causes a tendency to minimise their surface area, and hence volume [37]. Although often ignored, they are in constant flux with many gas molecules both leaving and entering bubbles continuously. Nanobubbles have raised cavity (Laplace) pressure, and grow or shrink by diffusion according to whether the surrounding solution is over- or undersaturated. Now, gas solubility is proportional to the gas pressure; this pressure, exerted by the surface tension, is in inverse proportion to the diameter of the bubbles and increases greatly at small bubble diameters. Any dissolution process is therefore accelerated, with an increasing tendency for gases to dissolve as the bubbles reduce in size [1,37].

Early theoretical calculations showed that nanobubbles should only persist for a few microseconds [38]. However, the ease with which water forms larger visible bubbles, under slight tensile pressure well below the tensile strength of water, and the greater difficulty that occurs on degassing, both indicate the occurrence of gas-containing nanobubbles (cavities). Clusters of nanobubbles (bubstons) have been proposed, which are stabilised by ionic solutes (and magnetic fields) [39] and contain gas at atmospheric pressure [40]. Nanobubbles in (still) mineral water can be magnetised and retain this magnetisation for more than a day [41]. A review of some hypotheses for the stability of bulk nanobubbles has been reported in the literature [42]. The likely reason for the long-lived presence of nanobubbles is that the nanobubble gas/liquid interface has a negative charge [43], which introduces an opposing force to the surface tension, so slowing or preventing the dissipation of bubbles. It should be noted that the liquid water surface has a strong affinity for electrons [43]. Curved aqueous surfaces may introduce a surface charge due to the water's molecular structure or its dissociation. It is clear that interfacial charge reduces the internal pressure and the apparent surface tension, with charge repulsion acting in the opposite direction to the surface tension. Similarly charged surfaces, together with the lack of van der Waals attraction (the cavities possessing close to zero electron density), tend to prevent nanobubbles from coalescing.

An additional stabilising effect to the charged interface is the slow rate of gas diffusion to the bulk liquid surface from both surfaces and bulk-phase nanobubbles [44,45]; in particular, nanobubbles in a cluster of bulk nanobubbles 'protect' each other from diffusive loss through a shielding effect [46], effectively producing a back pressure of gas from neighbouring bubbles separated by about the thickness of the unstirred layer. This slow dissolution will be even slower than might be expected due to the higher osmotic pressure at the gas–liquid interface, thereby preventing both gas dissolution and driving dissolved gas near the interface back into the nanobubble [46].

The classic Epstein–Plesset thermodynamic treatment of NBs [47,48] shows that NBs should not exist thermodynamically, and also gives rise to serious doubt as to their metastability and diffusivity in solution (especially in the case of bulk NBs) [48]. Indeed, there has been much controversy in the literature surrounding reasons why NBs, especially bulk ones, either do [49] or do not [50] have a degree of stability in pure water, and the present study does not concern itself with these fundamental existential questions: suffice to point out here that the present work takes the view that bulk NBs do exist unambiguously in practical situations of environmental significance, provided, of course, that they have been generated in a sufficiently robust manner (see Section 3).

## 3. Techniques for Nanobubble Generation

Bearing in mind the comparative lack of studies on techniques for nanobubble generation, as highlighted in Figure 1, a key challenge for nano-phase science and engineering lies in the discovery of simpler and easily-controlled generation methods. NB formation is often achieved when the homogenous liquid phase undergoes a phase change caused by a sudden pressure reduction below a critical value, known as cavitation [51–55]. Cavitation is commonly induced by the passage of ultrasonic waves (acoustic cavitation) [56,57] or by high-pressure variations in the flowing liquid (hydrodynamic cavitation) [58,59] or in chemical reactions such as electrolysis and conical-geometry approaches [60]. An intriguing new method involves the application of external static electric fields [61–63] (without electrolysis), based on electrostriction, which "sucks in" gas molecules at gas–liquid interfaces [64] This transient negative-pressure region established electrostrictively at the liquid–solvent interface allows for the development of "ultra-dense" NBs, which supports their observed greater lifetime [64] and belies the suggestion of a lack of stability of bulk NBs for times of practical interest [48,50].

In further detail, let us focus here on how the electrostrictive NB-generation method for ultra-dense NBs differs from other NB-generation approaches that involve electric fields to some extent, with most introducing electrolysis or foreign substances (e.g., ions) in the water. Differences between [64] and filed patents are listed below:

- Device for generating nanobubbles by electric current supply [65]

This approach uses water electrolysis, yielding water splitting to hydrogen and oxygen where the produced gases form nanobubbles.

- Water-containing oxygen nanobubbles and method for the production thereof [66]

Here, ultrasonic irradiation is used in conjunction with additive ions as a stabilising agent; this is totally different from my proposed method.

- Method of forming nanobubbles [67]

Here, electrolytes are added to the water. In contrast, my approach uses deionised water without any additives. Furthermore, a microbubble producer is used, whilst in my method, no microbubbles are needed.

- Method and apparatus for applying electrical charge through a liquid to enhance sanitizing properties [68]: this patent uses electrolysis with ionic sources.

## 4. Characterization of the Nano-Phase

In any event, despite discussing a selection of NB-generation approaches above, in the context of the scientific and technical breakthrough of the electrostrictive method in [64], a common feature of all previous types of "forced-convection" nano-phase generation approaches, is the potential confusion over bubbles, droplets, and particles being generated at the nano-scale by virtue of the mechanical wear and abrasion of moving parts [69] as detected in dynamic light scattering (DLS) and nanoparticle-tracking analysis (NTA). The unambiguous assignment of light-scattering species to bulk NBs is fraught with difficulty and scope for misinterpretation, as discussed by [48,69] with acuity and insight. Aside from (possibly not-always-reliable) DLS measurements, our ability to measure the presence of and characterize the properties of NBs with accuracy and confidence is limited. Surprisingly, few experiments have been conducted to quantify the total amounts of gas (in NBs and in solution) in a self-consistent way [69].

## 5. The Context for Nanobubbles in Environmental Sustainability

In sustainable chemistry, a key challenge lies in the creation of a new class of green solvents [70], especially those with characteristics that can be manipulated and tuned to be "tailor-made" for given applications (e.g., drug delivery) [71]. Of increasing interest, given the more stringent environmental-emissions regulations, are those that will have a more benign environmental fate in terms of avoiding air and water pollution, and harm ecosystems. With many pesticides being restricted and retired imminently for use (e.g., in the European Union and elsewhere) [72], the imperative to embrace greener and more sustainable liquids is gathering pace.

Applications of NBs have been proven to be beneficial in many environmental processes such as improved performance in water treatment [23], dyes [73], sterilisation by applying ozone gas [74], and in accelerating metabolism in shellfishes and vegetables [75].

There is considerable potential of NBs in soil remediation polluted by organic chemicals in combination with wider bio-remediation efforts [76].

Given this encouraging backdrop in applications for nanobubbles in ecology and in ameliorating environmental outcomes, we assess here—indeed “re-imagine”—the environmental and sustainable promise of liquids containing metastable bulk nanobubbles. Summarising the ‘state of play’ of nanobubbles in environmental engineering was our goal as well as offering a glimpse of the latest promising trends in more sustainable agriculture, and provide an outlook for important future NB developments to support the wider environmental-sustainability agenda.

Indeed, given this overall context and focus on environmental sustainability, one of the most important challenges lies in establishing facile and easily-controlled methods to promote NB formation to revolutionise vast swathes of science, agriculture, and technology (e.g., bolstering dramatically dissolved oxygen in the fermentation and wastewater treatment industry), or direct, seasonal gas storage in liquids, elevated far above normal (e.g., Henry’s-Law) solubility limits. Naturally, it is not easy to realise such applications because we need a deeper insight into the properties of nanobubbles. NBs exhibit several unique physical and mechanical characteristics such as smaller or virtual disappearance of buoyancy, extremely high surface area/volume ratio, zeta potentials, hydration [77], enhanced solubility of oxygen in water, generation of free radicals, protein coagulation and slow-rising velocity [10–12,78,79]. One of the peculiar quirks of NBs is that they can last for several weeks or longer with hydration [10,13,80]. The generation of NBs as well as characterisation of their interfacial properties and structure in water solutions is explained only tentatively with molecular-dynamics (MD) simulations and microscopy [64].

The disruptive development of facile, additive-free, and energy-efficient new methods of bulk-nanophase generation in solvents via local electrostriction ‘sucking in’ gas at transiently negative-pressure regions at the gas–water interface [64,81] allows for the exciting new possibility of using long-lived “designer” NBs to tailor, control, and manipulate the properties of solvents, indeed, for realising “nano-engineered” solvents. In the realm of “nano-gasification”, for example, adjusting the requisite amounts of NBs allows for regulating the viscosity, density, electrical conductivity, turbidity, and other properties. In turn, this allows us to contemplate the prospect of efficient and effective solvent-design strategies to optimise these NB properties for various applications (e.g., in the case of aqueous solvents, “nano-oxygenation” for activated-sludge water treatment [82], dissolved-air flotation [83], irrigation and fermentation [84] as well as the suppression of biofouling in the dairy and agricultural industries, and, powerfully, algal formation in water bodies (given the disastrous methane emissions therefrom whilst increasingly in eutrophic states [85]).

Given the low-energy, low-maintenance nature of this novel nanophase-generation approach [64,81], off-grid deployment via solar panels and batteries is an exciting and versatile “green-engineering” possibility for environmental sustainability (e.g., water-body management) (cf. Figure 2).

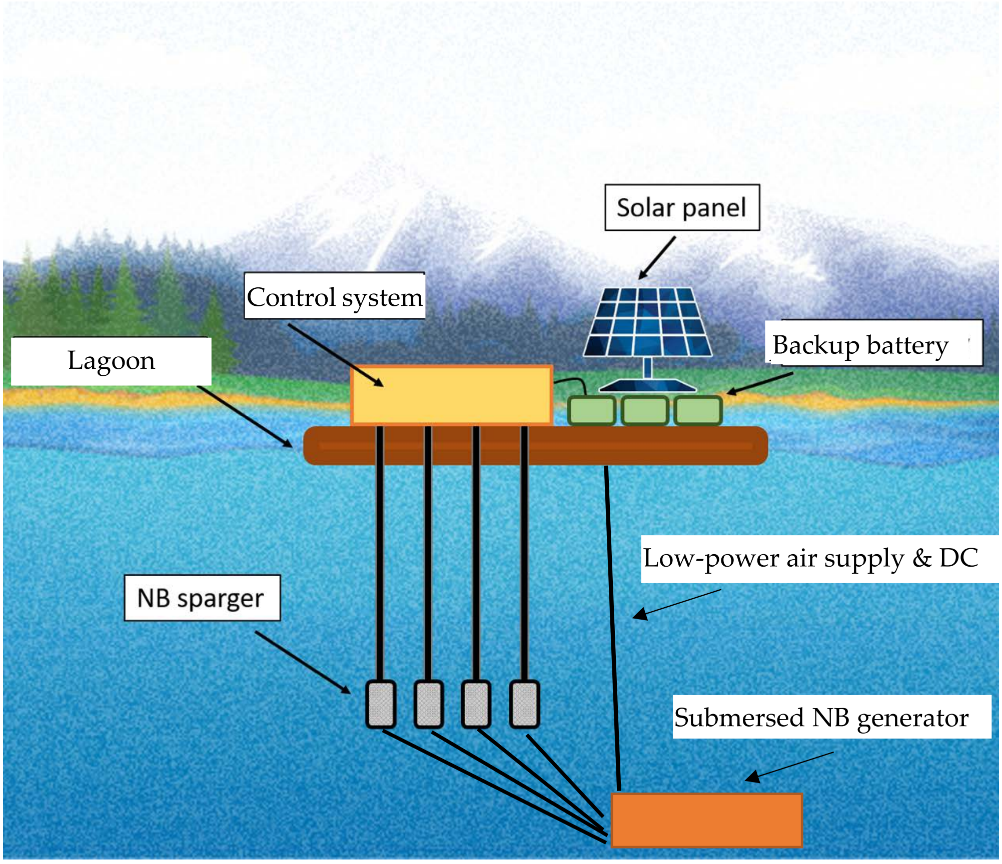

**Figure 2.** Concept of a submersible, lightweight, solid-state nanobubble generator (with no moving parts and low in maintenance) in the benthic-sludge region, using off-Grid power as per the floating-photovoltaics paradigm. Aside from favourable NB penetration to soften the benthic sludge and the associated biofilm suppression, the "nano-oxygenation" reduces the scope for eutrophication in the water body [85], which is important for mitigating methane emissions globally, in addition, naturally, to the suppression of algal blooms. A feedback-control loop can be employed for electric-field intensity variation in NB-generation and also regulation of bubble-release kinetics in a depth-calibrated way (e.g., by an on/off relay switch, sensitive to straightforwardly-monitored chlorophyll, and/or dissolved-oxygen measurements in the waterway). Naturally, multiple-input/output, Internet control via wireless connection may also be employed at higher cost (considering Internet-signal and bandwidth for data transfer). Image credit: altered from one supplied by M.R. Ghaani.

## 6. A Wastewater and Ecosystem-Management Pathway

As mentioned earlier, NBs have attracted significant attention in the last decade or two [3] due to their long-time (meta)stability and high potential for real-world applications. Amongst these applications, NBs can be applied towards nanoscopic cleaning [4,86,87] and water-field effects [88]. Turning to water and irrigation in agriculture and land-based ecosystems, as explained earlier, the phasing-out of agricultural pesticides in the present and near future [72] affords particular opportunities for ozone NBs in that they can act as a potent pesticide and simply degrade to oxygen in a slower fashion. This glimpse of aqueous-solvent design—NB-facilitated 're-thinking', as it were—offers a vision for sustainability in our management of ecosystems and environmental protection and remediation.

The lack of effective "enhanced-water" irrigation in arid regions is a major societal, agricultural and land-/water-management problem affecting food production, particularly in large, drought-laden tracts of the world, which is especially challenging in developing countries. Although it is not the purpose of this perspective to describe the wider problems of lack of potable water for mankind and the wider ecosystem and environment—or shortages of water at least clean enough for crop-irrigation purposes—it suffices to state that this is one of the grand challenges of the 21st century [89], as acknowledged by UN Sustainable-Development Goal 6—"clean water and sanitation for all". Around a quarter of the world's population is affected by water's physical scarcity, whilst a similar proportion face impending scarcity or economic shortage. Although there is enough freshwater for perhaps up to ten billion people by late-21st century population estimates [90], it is distributed very unevenly and much of it is polluted heavily, wasted, or managed in a poor and unsustainable way.

Therefore, improvements in the effectiveness and productivity of 'enhanced-water'/irrigation technology is key, and is at the core of addressing multiple UN Sustainable-Development Goals across food and water themes. Any such improvements in irrigation efficiency would need to encompass both traditional channel-through-soil delivery as well as more modern drip-feed and spray modes, which have become very popular in the Americas and Israel as well as in Southern Europe, Australia, Japan, and China. This will support glasshouse cultivation of protected crops.

Naturally, more such productive, higher-yielding irrigation water (or methods) would have a parallel benefit in boosting the growth of grass in arid regions, minimising (indeed, reversing) creeping desertification, thus assisting in overcoming a pressing and urgent land-management challenge in much of the world. In tandem with hydrogen management [91], this calls for the commercialisation [92] of more scalable, low-energy, additive-free nanobubble generation methods [64,81].

## 7. Case Study of Wastewater-Treatment

As a more detailed example of how NBs may be used to boost the performance and economics of wastewater treatment (WWT), let us consider the retro-fitting of a tank, in isolation mode, with NB-generation modules presenting an attractive proposition in terms of maintaining high DO levels (at the ~3 mg/L level beloved of activated-sludge bacteria) [6] with the NBs contributing to maintaining this level of DO (see Figure 3), where a retro-fit schematic is detailed below for such an arrangement:

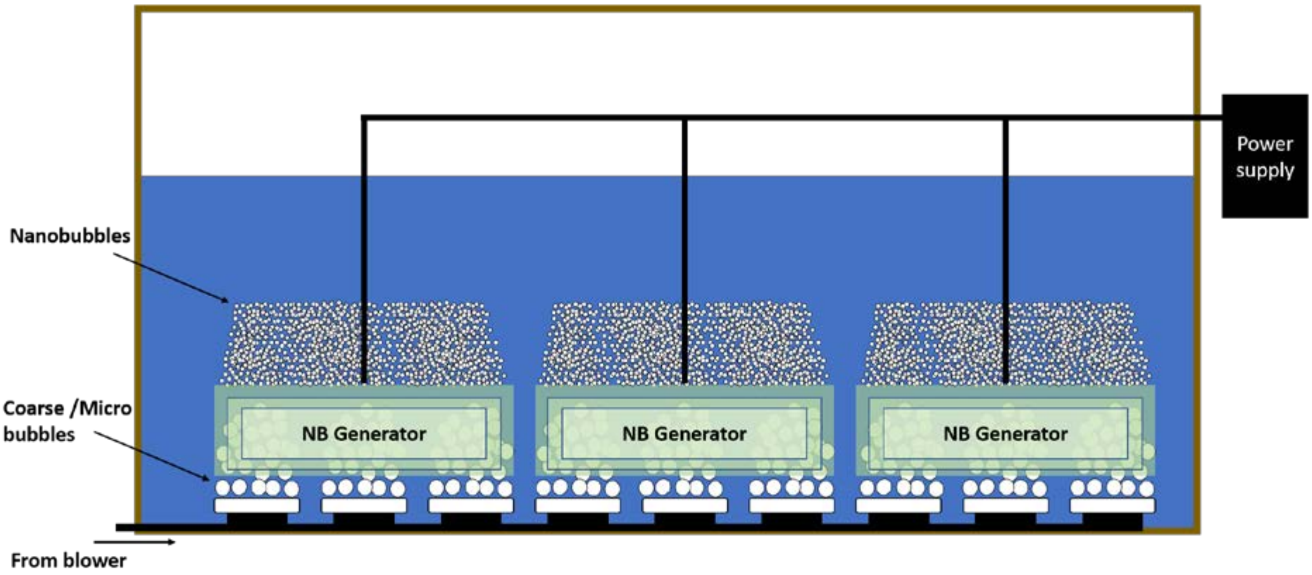

**Figure 3.** Retro-fit of the water-aeration tank with an existing bank of air diffusers. Image credit: M.R. Ghaani.

Using similar activated-sludge WWT economic-valuation approaches as in [6], it is possible to carry out a net-present-value (NPV) analysis of conventional aeration approaches with blowers (typically at 50% of nominal capacity and 25 Hz) and take into account how NBs, and especially ultra-dense ones [64,81], can increase both the oxygen-transfer rate and the aeration efficiency [6,64,81]. Figure 4 depicts a NPV-based cost comparison between

NB and existing aeration as a function of how clean the water is to be. It is clear that this does not scale linearly with the level of cleanliness for established aeration, and that NB approaches are far more energy-effective and essentially linear-scaling with the level of cleanliness required.

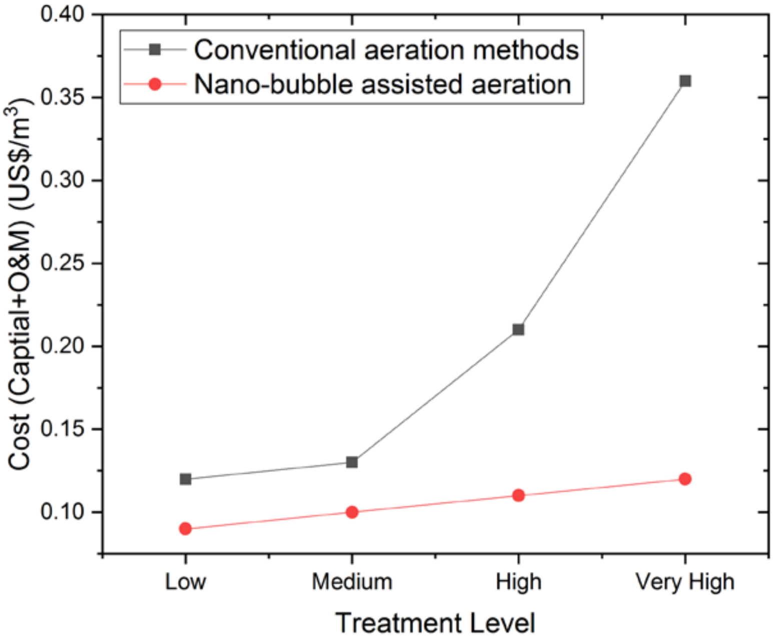

**Figure 4.** The total cost (rolled-up CAP- and OP-EX) of wastewater treatment as a NPV, which depends on the technological aspects as well as the water quality to which the water is treated. Treatment costs increase exponentially with improved water quality, with respect to established aeration approaches. Black curve: Cost of wastewater treatment for increased output. Low: BOD >60 mg/L; Medium: BOD 20–60 mg/L, TSS 30–90 mg/L; High: MBTP, BOD, and TSS levels of 20 and 30 mg/L, respectively. Red curve: Refers to the cost estimation of innovative ultra-dense NB technology, [64,81], which provides an essentially linear scale vis-à-vis treatment level. Image credit: M.R. Ghaani.

## 8. Agricultural Progress and Visions

In recent years, various studies have outlined the effects of micro- and nanobubbles in water on promoting the physiological activity of living organisms (e.g., plant growth [93–95], fish [96,97] and cell cultures [98,99]), albeit without providing a mechanistic detail on how NBs promote these effects. One reasonably plausible theory, in the case of spinach, hinges on NBs' putative promotion of reactive oxygen species, with a promotional effect by exogenous ·OH radicals [95]; however, in the case of carrots, the NB-promoted ·OH-radical concentration was in excess of a toxic threshold [95], resulting in no enhancement in carrot yields (and quite the opposite).

In any event, in terms of a useful working hypothesis, [95] pointed to the indication that it is actually oxygen-NB transport into (plant/crop) cells, and localised *intra-cell* NB concentration effects may either promote, or not, seed/plant germination and growth. An unreported aspect of the literature on NB-enhanced physiological processes is the important matter of NBs being sufficiently small to allow for their facile transport across plant–cell boundaries, with NB diameters typically needing to be below about 150 nm for this to be routinely possible. Clearly, the overall *de facto* dissolved-oxygen (DO) concentration is important, with general observations that plants favour DO levels of circa 12–14 mg/L [33,34], whilst the Henry's-Law DO level is about 8.5 mg/L for air at ambient pressure, although most irrigation water routinely has DO levels of only 4–6 mg/L.

Motivated by the positive role that NBs have to play in agriculture and food sectors, we have applied such "nano-bubbly" deionized (DI) water, supplied from an Aqua-B

NB generator from both $O_2$ and ambient air (of average diameter of ~95 and 90 nm and populations of ~6 and $4 \times 10^8$ per mL, respectively) to "proof-of-concept" seed-germination studies. Here, we put 5–6 watercress seeds each in 24-slot tray (cf. Figure 5) with roughly 65 mL of peat moss in each slot, and we added ~15 mL of DI water to each slot in one case (cf. Figure 5, left) and the same volume of water with ~21 and 12 mg/L of total (conventionally- and nano-)dissolved oxygen, respectively, and over-saturated in the latter case by $O_2$ in the form of nanobubbles "drawn in" from air by electrostriction [64,81].

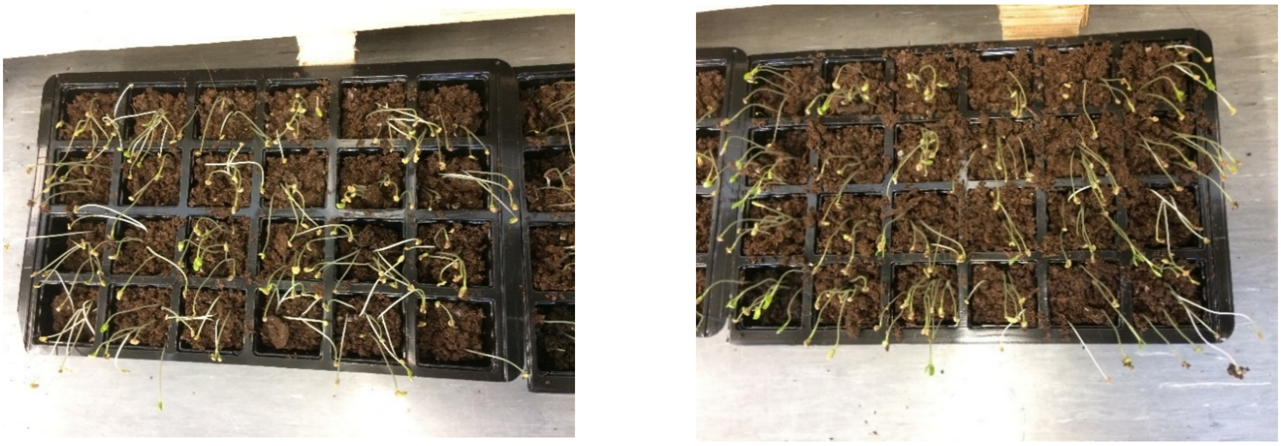

**Figure 5.** Typical top view after seven days of watercress germination with deionized water. (**Left**) Conventional DI water. (**Right**) With NBs drawn in from air.

After seven days, there was ~35 and 21% enhanced seed germination growth for $O_2$ and air "nano-bubbly" water, respectively, vis-à-vis DI, averaged over 24 cases for each scenario, in terms of mass of shoots; to a much lesser extent, the number of shoots was enhanced (just by ~7 and 5%, respectively). One-tailed Student's *t*-tests gave 90%-confidence $H_0$ rejection on a shoot-mass basis for $O_2$ NBs (at circa 93%), and almost for air NBs (89%). Although promising, further tests are needed to establish *prima facie* evidence of clear-cut seed-germination promotion for more plants and leafy greens afforded by air NBs on larger-scale field trials. Clearly, different crops will benefit to a greater or lesser extent from root-delivered NB aeration at various distinct stages of their developmental cycles, which is already well understood in classical "smart-irrigation" systems [92].

With this tentatively-suggested effect of enhanced physiological effects for root-delivered seed germination afforded by the action of NBs drawn simply from the air (as opposed to pure/near-pure, higher-pressure $O_2$, e.g., from cylinders or oxygen concentrators) sufficiently small to penetrate through the cell–wall matrix, there is much scope to revolutionise agriculture, especially using off-grid NB generation from solar panels. Once again, reprising the role of NBs as delivery agents in medicine [100], the prospect of leveraging NBs, whether of air, $O_2$, or $CO_2$, as templates upon which select nutrients or agents can be delivered phytogenitically (e.g., via roots or stomatally) [100] in a targeted way using precision-irrigation and smart-agriculture methods (such as satellite and/or plant-feedback responses) [92], constitutes an intoxicating vision by which to transform the delivery effectiveness of nutrients. Furthermore, slow release of these agents in vivo by virtue of strong adsorption to the NB surfaces, coupled with saving both water and growth-agent usage, allows for 'smart' liquidity to indeed be re-imagined. Again, as in the off-grid visions of Figure 2, the deployment of satellite and/or wireless Internet 'intelligence' allows for trivial feedback (or even feedforward) control loops, and to be deployed, whether low- or "high"-tech (e.g., simple 'off-line' local feedback control by on/off relay switches, or feedforward control via advanced neuromorphic-aware software algorithms delivered via the Internet).

In any event, aside from straightforward engineering-control-loop approaches *per se*, the cultivation of industrially- and environmentally-useful algae by $CO_2$ NBs, together with their enhancement of tree and grassland growth serves, in tandem, to cut carbon emissions to the atmosphere as well as preserving ecosystems. Not only will NBs transform agri- and aqua-culture, *inter alia*, but also (grass-)land and water management.

## 9. Environmental and Sustainability Outlook

Up until now, NBs have been little used in practical applications due to the high energy cost of traditional "forced-convection" approaches in their generation, the inevitable bio-fouling of associated membranes, and their (and the mother-solvent's) impurity-laden nature [3,92]. However, given the electrostriction approach to the generation of the nano-phase [64,81], the real competitor to this new approach is the *status quo* (*ante*) of conventional bubbling, whether coarse or fine. In any event, in terms of commercialisation outlook, a key driver for market adoption of NB-generation technology lies in retro-fitting existing systems (e.g., in adjusting air-delivery diffusers (already *de facto* small-bubble generators) in wastewater-treatment (WWT) and recirculation-aeration systems (RAS)), allowing for more facile generation of NBs by DC electric fields [64,81]. A quantitative assessment of various key metrics of NB effectiveness is also warranted for investigation, with just a few of the more prominent ones listed in Table 1 (with "nano-aeration" in mind, but in general towards other gases). This will allow for the most appropriate and scalable NB-generation approaches to be leveraged towards the environmental end applications.

**Table 1.** Several obvious competitive performance metrics for assessing NB generation.

| Competitive Performance Indicator | Value |
|---|---|
| Bubble lifetime: exponential-decay half-life | Minutes to months, depending on gas/solvent type |
| Energy cost of Aqua-B NB generators | kW/kg $O_2$ transferred/h |
| Aeration efficiency (AE) | kg $O_2$/kWh |
| "Bubbles per buck"—energy cost per kg gas in NBs | W/mg/L |

The adoption of high-level policy drivers and associated government financing for the environment such as sustainability in climate-, food-, and water-resourcing (e.g., with the EU's venerable "Green Deal" and "Farm-to-Fork" initiatives and the World Bank Environment Strategy) shaped, motivated, and informed by the UN Sustainable-Development Goals, is changing the economic calculus of rendering "public-good" valuation more efficiently, allowing greater scope for "environmental industrialism" [92]. Combining NB generation with drip-feed irrigation [92], especially for in-line pipe-based models using electrostriction [64,81] supplied simply by atmospheric air and off-grid solar energy (cf. Figure 2), will be a disruptive innovation that will boost aeration for in-field crop growth (cf. Figure 3), and progress here can be leveraged and delivered rapidly to WWT (municipal, agricultural, and industrial) and RAS in aquaculture, together with water-body management and nano-aeration as well as grassland and forest cultivation in ecosystem management. This will usher in a new era in NB-facilitated environmental engineering and sustainability.

## 10. Conclusions

This review and perspective has argued that technical and commercial mastery of nanobubble generation, combined with vision and panache in "green-thinking", serves as a potent tool and force for good in the re-purposing of water and aqueous solvents for a more sustainable world, in keeping with Man's wider sustainable and moral responsibilities to nature and the Earth, as reflected in the current governments' "green-policy" agendas and regulatory and public-economics drivers.

Turning to specific and key benefits flowing from this environmental-applications vision, one must reflect on the key and tantalizing possibility of the nano-phase, and more specifically ultra-dense NBs, serving as delivery agents [100], or "nano-carriers", enabling us to deliver this green vision (pardon the pun!). Here, nano-carriers are universally considered as a new frontier for therapeutic delivery of various types of bioactive molecules, assuming them to be the archetype of specific, effective, and safe therapy, which is especially exciting in the plant kingdom. Acoustically-driven bubbles continue to find new therapeutic uses including drug delivery to tumours, opening the blood–brain barrier, and direct fractionation of tissues for surgical applications as well as the exciting prospect of controlled delivery inside plants (for delivery either through roots or stomatally [101]). Creating acoustic cavitation at length scales and pressure amplitudes compatible with animal, grass, tree, fish or plant biology remain a major challenge, which could be greatly facilitated by a new generation of nano-scale cavitation nuclei that stretch our current understanding of nanobubble stability, acoustic microstreaming, and the interaction between cavitating bubbles and biological media [101].

In the literature on the application of nanobubbles as carriers to enhance stability under ultrasound exposure, an extra layer has been added over the gas core. As a result, two main types of nanobubble components are present with different physico-chemical characteristics, namely for the inner core and for the outer shell. The shell mainly comprises surfactants, polymers, or proteins, while the core air contains sulphur hexafluoride and perfluorocarbons. Safe, biocompatible, biodegradable, and regulatory admitted substances should be selected for the system formulation. It has been hypothesised that remnant shells shed into the surrounding aqueous medium, folding into liposomes or micelles [100,101], and similar ideas have been expressed for plants [100]. Therefore, a specific benefit of ultra-dense NBs lies in the exciting vision of NBs as targeted nano-carriers and release agents.

Nanobubbles can be loaded with gases, small molecules, and macromolecules, either hydrophilic or lipophilic. Different technological approaches have been proposed to associate molecules within the bubble structures, exploiting design strategies previously tuned for micro-bubbles. Three loading types are generally possible. Drugs might be encapsulated within the core, or they might be incorporated within or just beneath the nanobubble shell. In addition, encapsulation of the drug or delivery agent in a nanoparticle subsequently attached to the bubble surface is another approach to loading for release inside the fish, plant, grass, tree or animal as a health-delivering/enhancing and specific beneficial treatment [100,102].

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