Nanosensors for Water Quality Monitoring

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ABSTRACT

Nanomaterial enabled sensors are being designed for high efficiency, multiplex functionality, and high flexibility sensing applications. Many existing nanosensors have the inherent capacity to achieve such goals, however, they require further development into consumer and operator friendly tools with the ability to detect analytes in previously inaccessible locations, as well as at greater scale than heretofore possible. Here I discuss how nanotechnology enabled sensors have great, as yet unmet, promise to provide widespread and potentially low-cost monitoring of chemicals, microbes, and other analytes in drinking water.

MAIN TEXT

Throughout history the quality of water for consumption has been monitored to minimize exposure to disease causing agents. The ancient Romans, for example, recognized the need for high quality water with the architect and civil engineer Vitruvius noting in his \textit{de Architectura} that water composition depends on ‘the quality of the earth’ through which it flows or is collected and that water quality can be ascertained either by assessing the physical attributes of the people who consume the water or by visually measuring its corrosivity towards brass\textsuperscript{1}. Over the intervening centuries, we have progressively improved our capacity to detect water
contamination. Across much of the world, the water that comes out of the tap is clean and fit
for consumption. This story, however, is not universal. Shockingly, there are more than 844
million people without access to safe drinking water\(^2\), and nearly 2 million, primarily children
below age 5, who die every year due to a lack of access to safe drinking water. Under the aegis
of the UN Sustainable Development Goals (and the Millennium Development Goals that
preceded them) these numbers are declining, but climate change, increasing local and global
population pressures, rural to urban human migration, under-investment in infrastructure, and
the concomitant declines in water availability make further improvements increasingly
daunting.

Water quality monitoring, both at large and small scale, is challenging due to the variability
and complexity of the matrix and the low concentrations of pollutants that need to be
detected. In recognition of these issues, nanomaterial-enabled sensor platforms have received
increasing levels of attention from the research community ever since the first promising
reports of nanowire\(^3\) and quantum dot\(^4\) enabled sensing. Owing to their novel properties,
nanomaterial-enabled sensor platforms for water quality promise ultralow multiplex detection
and rapid analysis times\(^5\-\(^7\). While there continues to be great excitement in the laboratory and
in the literature about nano-enabled sensors, to date only a few such sensor devices (e.g.,
RapidChek\(^\text{®}\), Watersafe\(^\text{®}\)) have made it to market, and the societal impacts of this line of
research have fallen short of its initial promise. The question this Perspective seeks to address is
what should the next directions be for the nanosensor field – particularly with respect to water
quality monitoring. Herein, I summarize the current state of nanotechnology enabled sensors
for water quality monitoring, discuss potential focus areas for nanosensor application within
the water monitoring arena, and then conclude with some final considerations.

Nanotechnology-enabled sensors

The word sensor stems from the Latin word *sentio*, which means to perceive or observe. In
the context of water-quality monitoring, sensors respond to the presence of a contaminant or
analyte and provide output that can be interpreted by an end-user. Over the centuries,
humankind has moved beyond its five basic senses and developed a suite of water quality
sensors to detect pathogens, organic and inorganic chemicals, and other water quality
parameters (e.g., pH, hardness [the amount of dissolved calcium and magnesium in the water],
turbidity [the cloudiness of the water]) with the ultimate purpose to protect users of a
particular water. Such sensors may be centrally located within a water treatment plant, found
within a distribution system, or even located at the point of use (POU). They can be on-line,
evaluating the quality of the water as it flows past, or off-line and used to evaluate grab or
composite samples. At the present time, most methods for the detection of regulated
contaminants (Table 1) involve collection of periodic samples that are evaluated off-line using
chromatographic and spectroscopic methods for organic and inorganic chemicals and a range
of approaches for coliforms, fecal coliforms, *Giardia, Cryptosporidium, Legionella*, and viruses.

Nanotechnology enabled sensors have the capacity to replace many existing water quality
sensors. Others have explicitly differentiated the terms nanoprobe and nanosensor, noting that
a nanosensor measures an analyte and requires rapid and reversible binding, while a
nanoprobe selectively detects microbes or chemicals with high sensitivity, but does not require
reversibility nor is it quantitative. For simplicity, herein, I utilize a holistic definition and use
the general term nanosensor to reflect any sensor platform that utilizes the unique optical, electrical, or magnetic properties of a nanomaterial to enhance analyte detection. To date a broad range of nanosensors have been proposed for the sensitive detection of pH, pathogens, and toxins in water\textsuperscript{9-12}.

At the most basic level a nanosensor consists of 1) a nanomaterial, 2) a recognition element, and 3) a mechanism for signal transduction\textsuperscript{13}. Analytes of interest interact with the recognition element and induce a detectable signal that can be acquired\textsuperscript{12}. Nanosensor specificity is achieved either by detecting an intrinsic signal from the analyte or by employing highly specific recognition elements that ideally bind only to a given target. The sensitivity of a nanosensor arises as a function of the novel optical, electrical, or magnetic properties of the nanomaterial itself as well as the signal transduction method used to generate a signal following association with an analyte. Figure 1 illustrates representative nanosensor architectures for environmental analyte detection.

The literature contains numerous reports of extremely low detection limits for many nanosensors; however, such detection limits are often not verified under realistic conditions that reflect water quality in the field. Furthermore, because of the small scale of a typical nanosensor platform, ensuring the association of an analyte with the sensor interface is a non-trivial consideration. Such is particularly true for biological particulates such as bacterial cells, viruses, and protozoa that may be dangerous at concentrations as low as a single organism or virus particle and that have similar or larger dimensions than the sensor. For these types of analytes, sample pretreatment (i.e., purification or concentration) may be required for optimal nanosensor deployment. Potential approaches to pretreatment include rapidly developing
methods such as microfluidic separation\textsuperscript{14,15} and nanoparticle based isolation\textsuperscript{16} as well as more standardized filtration\textsuperscript{17} and centrifugation based methodologies. Sample pretreatment is a focus area for many sensor research laboratories and is not discussed in detail here.

Nanosensors can be classified based upon the types of nanomaterials they contain, the analytes they detect, and the signal transduction method employed to monitor analyte recognition. For simplicity, I utilize the latter and explicitly only discuss nanosensors that rely upon the most broadly applied signal transduction methods: optical, electrical, and magnetic.

Table 2 summarizes the variety of nanomaterials employed in water quality nanosensors.

Detailed descriptions of the many types of nanomaterials employed within nanosensors can be found elsewhere\textsuperscript{10,18-21}.

**Optical signal transduction.** In an optical sensor, a signal is produced when the target analyte interacts with a nanomaterial. This approach is highly popular due to its general simplicity of operation, rapid readout, and practical sensitivity. Fluorescence and surface plasmon-enabled spectroscopies are the dominant optical signal transduction approaches.

Fluorescence is based on the measurement of the emission of a fluorophore when it returns to its ground state following light excitation\textsuperscript{22}. Fluorescent nanoparticles such as quantum dots, metal nanoparticles, and upconversion nanoparticles are being investigated for their sensing applications. Many of the interesting developments in the use of fluorescent nanoparticles for sensing applications were recently summarized by Ng et al.\textsuperscript{21}.

Noble metal nanoparticles, such as gold and silver, when excited by light can support surface plasmons (e.g., coherently oscillating surface electrons) that generate strong electromagnetic fields within the vicinity (i.e., within several nanometers) of the nanoparticle
The frequency at which the surface electrons resonate results in an absorption band that is referred to as the localized surface plasmon resonance (LSPR) that is a function of the size, shape, identity, and local environment that surrounds the nanoparticle. Two categories of signal transduction utilize LSPR: surface-enhanced Raman spectroscopy (SERS) and colorimetric (absorption) methods. LSPR generates an enhanced electromagnetic field in the vicinity of the noble metal surface. When target analytes are within this enhanced electromagnetic field, their Raman cross sections are increased by several orders of magnitude – this enhancement is known as SERS. Because SERS is a vibrational spectroscopic method, a SERS spectrum reflects the characteristic covalent bonds of the analyte. If the signal from this ‘fingerprint’ spectrum is sufficiently intense it can be directly evaluated to indicate the presence of an analyte in a complex matrix. In this intrinsic detection mode, SERS has shown the capacity for single molecule detection\textsuperscript{24}, albeit typically for non-environmentally relevant analytes under demanding instrumental operating conditions. The application of SERS for water contaminant quantitation is complicated by the requirement that the ‘hot spots’ primarily responsible for the SERS enhancement are typically < 5 nm in size and thus large analytes are size excluded\textsuperscript{20}. This fact coupled with the requirement that the analyte must associate with the noble metal nanoparticle surface can hinder the use of SERS for intrinsic analyte sensing. The alternative, and more widely applied approach, is to functionalize the nanoparticle surface with affinity ligands such as antibodies and aptamers\textsuperscript{25}. Highly sensitive, hand-held Raman spectrometers are increasingly affordable and thus it is likely that SERS will progressively come to occupy a
larger portion of the nanosensor armamentarium due to the high sensitivity of the method and its multiplex capacity\textsuperscript{26}.

Colorimetric sensing is a simpler manifestation of LSPR and typically involves the monitoring of nanoparticle aggregation state. Destabilization of nanoparticles results in color changes (generally red$\rightarrow$blue for spherical gold nanoparticles; yellow$\rightarrow$brown for spherical silver nanoparticles) that reflect the coupling of surface plasmons on adjacent particles. These color changes can be monitored either visually or by using a spectrophotometer. A number of aggregation based assays for water borne chemicals and microbes have been reported (\textbf{Table 2})\textsuperscript{19}. Such assays can be made field deployable by their incorporation into low-cost paper-based colorimetric assays\textsuperscript{15}.

\textit{Electrical signal transduction}. Electrical signal transduction takes advantage of the high conductivity and electrochemical stability of silicon, noble metal nanoparticles (Pt, Ag, Au), carbonaceous nanomaterials (graphene, carbon nanotubes), and inorganic 2D nanosheets. Nanosensors relying upon electrical transduction fall into three categories: chemiresistors, field-effect transistors, and electrochemical sensors\textsuperscript{10}. Chemiresistors consist of an electrical circuit whose resistance is altered when an analyte interacts with the sensor surface. Field-effect transistors (FETs) measure the mobility of a charge carrier (i.e., analyte) moving through a channel subjected to an applied electric field controlled by a conductive gate electrode. When an analyte enters the channel, a change in signal is detected. FET based nanosensor platforms have been in development ever since the pioneering studies of Cui and Lieber in 2001\textsuperscript{3}. Electrochemical sensors measure voltage or current changes that arise following an electron transfer reaction between the sensor surface and a target analyte or intermediate. The
modification of chemiresistors, FETs, or electrochemical sensors with recognition elements (antibodies, aptamers) has enabled sensitive detection of waterborne contaminants such as *Escherichia coli*\(^{27}\), *Hepatitis C*\(^{28}\), and many others.

**Magnetic signal transduction.** Magnetic nanomaterials exhibit the capacity to respond to an external magnetic field, and the functionalization of such nanomaterials with analyte specific biomolecules provides the ability to magnetically isolate analytes that can then be detected\(^{29}\).

Nanoparticle design is dependent upon the ultimate application, with nanoparticle size and chemical identity dictating particle magnetism. A range of materials are used to produce magnetic particles and include metallic iron, oxides of iron, cobalt, nickel, and a variety of multielement materials. Iron-based nanoparticles (e.g., Fe\(^0\), Fe\(_3\)O\(_4\), γ-Fe\(_2\)O\(_3\)) are of particular interest due to their perceived biocompatibility and lower cost synthesis.

Magnetic signal detection strategies fall into three general categories: 1) magnetoresistance, 2) hydrodynamic property measurements, and 3) T\(_2\) relaxation nuclear magnetic resonance. Magnetoresistance sensors exhibit changes in electrical resistance following the binding of magnetic nanoparticle labeled analytes and have recently been used for the detection of *Mycobacterium bovis*\(^{30}\) and Influenza A\(^{31}\). Changes in hydrodynamic properties that result from analyte induced nanoparticle clustering can be detected by monitoring nanoparticle relaxation dynamics in a time-dependent magnetic field. A field-deployable application of this approach has been used for *Bacillus globigii* spore detection\(^{32}\). Magnetic resonance imaging can be used to monitor the change in the T\(_2\) (e.g., spin-spin) relaxation time of water protons that occurs when magnetic nanoparticles aggregate in the
presence of an analyte. Such an approach has been taken to sensitively detect both *Salmonella enterica* and Newcastle disease virus (as a representative virus)\(^3\)3.

When do nanosensors make sense for water quality monitoring?

A key issue that is too often forgotten in the rush to develop new and novel nanosensors is the *a priori* consideration that they will address either a current unmet need or that they will outperform established approaches. Prior experience has shown that the ultimate utility of any new technology is dependent upon its ability to either provide improved capacity or to address current gaps in device function\(^3\)4,\(^3\)5. Given the historically conservative nature of the water treatment community\(^3\)6,\(^3\)7 these concerns must be considered in the earliest stages of nanosensor design. Continued advancement of the applied nanosensor field requires focus on applications where nanosensors truly provide novel capacity or added utility. In the context of water quality monitoring, I suggest three potential focal themes:

1) *Improved monitoring of water distribution networks.*

The current approach to water supply in much of the world relies upon centralized treatment and distribution\(^3\)8. Under this paradigm, water is treated at a centralized plant using a number of physical and chemical processes (with the exact combination a function of the initial quality of the water being treated) prior to distribution. In many countries, a residual disinfectant is added immediately prior to water leaving the plant to minimize pathogen concentrations. Within the distribution system, treated water can be subject to intrusion by waste-, surface-, or ground-water and its quality can be degraded due to the leaching of contaminants (e.g., lead, copper, polymers) from plumbing materials or by bacterial re-growth\(^3\)9. Water treatment plants, water towers, and water taps are readily visible
components of centralized treatment systems; however, their relative importance as sampling locations can be dwarfed by the large volume and spatial diversity of the drinking water distribution system and the pipe networks within buildings (Figure 2). This hidden infrastructure comprises a highly complex engineered ecosystem whose characteristics are affected and defined by operational and environmental parameters in ways we currently do not fully understand. In centralized treatment systems, discrete numbers of water quality samples are routinely collected either at the treatment plant, at selected points within the distribution system, or occasionally within buildings (i.e., ‘premise plumbing’)\textsuperscript{40}. This sampling approach potentially misses regions of concern that arise due to differences in geography, water age, or other factors that may not have been considered in the design of the sampling scheme. Furthermore, such approaches can lead to biases, either inadvertent or purposeful, that misrepresent overall water quality. For example, in the Flint, Michigan lead crisis it was documented that the water treatment staff did not sample enough homes with known lead service lines, even though it was legally required as those homes represent the greatest risk\textsuperscript{41}.

The development of the Internet of Things (IoT)\textsuperscript{42} promises deployment of sensor networks that acquire real-time data from sensor nodes across widely distributed areas. This concept is particularly appealing for water supply and management\textsuperscript{36,43,44} as these sensor networks would potentially enable a more detailed understanding of the chemistry and biology of distributed water all the way from the water treatment plant to the tap. One intriguing possible future for the IoT is the incorporation of networks of nanosensors into an Internet of Nano-Things (IoNT) that interconnects nanoscale devices and connects to the IoT\textsuperscript{45-47}. In the context of water distribution, such a network would consist of an integrated array of nanosensors that would
provide real-time monitoring of water quantity and quality both at fine-grained temporal and geographic scales and at locations throughout the distribution system that are inaccessible to existing approaches (e.g., dead-end pipes; connections between service mains, service lines, and premise plumbing; within biofilms; in showerheads, etc...; Figure 2). The IoT is rapidly evolving and it is broadly recognized that there remain many challenges that must be overcome with respect to data collection, data communication, data storage, and device power to make this vision a reality. Integration of embedded nanosensors into water infrastructure will clearly require considerable nanosensor optimization. Many of the nanosensors that have been developed to date (Table 2) will need to be reconfigured and redesigned to 1) enable device operation under highly variable environmental conditions, 2) simplify in-field sensor replacement, 3) facilitate data communication, and 4) minimize the potential for sensor fouling. This latter issue should be a particular focus for embedded sensors for which fouling by salts, organic matter, and biological growth must be accounted for in the earliest stages of development. In addition to addressing these and other technical issues, it is equally imperative that the development of distributed water quality monitoring networks be done with utmost consideration for data security and data privacy. If an IoT connected system of nanosensors is to be deployed within a distribution system then the pertinent regulatory requirements must be considered as early as possible in the design process. A key aspect of the final assessment will be to show that the nanosensors are stable and do not degrade. In particular, the potential for nanomaterial release from the integrated nanosensors during their use should be considered along with the potential health implications of any subsequent exposures.
Assuming that all of the technical and social issues facing the development of the IoT platform can be met, the data collected from suites of integrated nanosensors would revolutionize our understanding of the intricate ecosystems present within drinking water distribution systems. Recent advances in offline microbial and chemical sensing have already revealed highly complex multifaceted relationships between the physical components of the drinking water distribution system, the chemistry of the water flowing through it, and the microorganisms that reside both within the water as well as adhered to pipe walls. Coupling the knowledge potentially gained through the application of artificial intelligence and machine learning with data collected in real-time at scale would only help to further crystalize this understanding.

2) Detection of non-target, unregulated analytes.

The reuse, or recycling, of wastewater as a potable water supply source is becoming increasingly common in many parts of the world as a result of climate change, increasing local and global population pressures, and human migration[^1]. With increased reuse, there is a concomitant increase in the likelihood that wastewater derived biotic and abiotic contaminants may end up in treated drinking water. For example, studies have found increased levels of Cryptosporidium, Giardia, and Legionella in water distribution systems fed recycled water[^2], and there are many concerns about the potential for increased dissemination of antibiotic resistance by reused water[^3]. Finally, with amplified water reuse there are growing concerns about the possibility that many currently unregulated and challenging to detect ‘emerging’ organic and inorganic chemicals will be present in treated water. Currently, there are an estimated 85,000 chemicals used in commerce in the US and approximately 140,000 in the
These chemicals include broad classes of compounds with known or suspected toxicity such as chlorinated paraffins, fluorinated compounds, nanomaterials, micro- and nano-plastics, and flame retardants. While it is unlikely that all of these chemicals will be present in treated water, it is unclear which compounds are most likely to be present. This lack of knowledge reflects the sheer numbers and quantities of chemicals being used as well as a lack of knowledge of how they are being used.

Current approaches for water quality monitoring are generally reliant upon protocols that are necessarily skewed towards regulated contaminants (Table 1). Separate protocols are required for different chemical contaminant classes (e.g., metals, volatile organics, semi- and non-volatile organics) as well as microbial contaminants (e.g., viruses, bacteria, protozoa). In the case of bacteria, these protocols focus on detection of indicator bacteria such as *Escherichia coli* and fecal coliforms. So long as these indicators are present at levels below the regulatory limit it is assumed that pathogenic bacteria are also below levels of concern. Unfortunately, these indicators are completely unrepresentative of disease causing strains and thus their absence does not necessarily ensure pathogen-free water.

Many analytes are difficult to detect by existing approaches (i.e., unculturable organisms, small-highly soluble organics, antibiotic resistance genes). While the development of highly specific nanosensors to detect each and every potential contaminant would be cost and time prohibitive it is nonetheless reasonable to advocate for the development of nanosensors targeting emerging pathogens (*Legionella* spp., *Naegleria fowleri*, enterovirus) and chemicals with known toxicity. The decision as to which analytes to target should be a primary consideration in the earliest stages of device development. Simply designing another
nanosensor for *E. coli* or Pb$^{2+}$ ion, while potentially intellectually stimulating, may not ultimately be useful if sensors are not simultaneously being developed for higher-priority targets. One promising nano-enabled approach going forward would be to develop semiselective methods that rely upon pattern recognition$^{52-64}$. Recent efforts have focused on the development of array based ‘chemical nose’ or ‘chemical tongue’ sensors that employ selective analyte recognition. The interaction of any given analyte with the array is used to develop a selectivity-based pattern. In this way, the combined response across the sensor array is then assessed using multivariate statistics. While such an approach with nanosensors has yet to be applied for water quality monitoring, it has found success in disease detection. Recently a nanoarray was able to determine disease from exhaled breath$^{64}$. Determination of disease occurrence for 17 different disease types in a patient population of over 1400 people was achieved using an ‘artificially intelligent’ nanoarray composed of molecularly modified gold nanoparticles and a random network of SWCNTs. Given the ever-expanding number of identified contaminants in drinking water such an approach could have great value as it could be trained to potentially detect species that are currently not regulated (i.e., nitrosamines) and thus are infrequently quantified. Furthermore, such an approach could be particularly useful for detection of volatile and semi-volatile contaminants through the development of gas sampling systems that monitor the head-space above water samples either on- or off-line. Such a design would help to minimize sensor fouling.

The complexity in the types and concentrations of potential contaminants suggests an alternative approach that is less focused on individual contaminants and more on groups of contaminants. Recent developments in nontarget screening (NTS) using high resolution mass
spectroscopy illustrate the sheer number of analytes present within aquatic matrices. In the face of this complexity and the sheer volume of data being collected by NTS approaches, the NTS community, similar to the proteomics and metagenomics communities before it, has begun sharing data analysis methods, spectral databases, and is actively discussing the future of NTS. The nanosensor field should learn from these prior success stories and work in as collaborative a manner as possible to ensure cross-platform compatibility that will rapidly advance the field.

3) The democratization of water quality sensing.

Centralized, large-scale water treatment is economically viable in areas with high population densities and with the capacity to build and maintain the necessary infrastructure for treated water distribution. However, in rural areas and in countries and regions with insufficient resources for construction and maintenance such centralized facilities are impractical. Furthermore, efforts to increase local resiliency against droughts and other disasters have led to a growing emphasis on decentralization. For these reasons, de-centralized or POU based water treatment is increasingly being considered a viable treatment approach. POU designs range in design from simple low-cost filters to more complex and costly engineered designs employing nanoparticles or engineered filters. Current estimates suggest that the POU marketplace exceeds $20 million annually, a fact supported by the observation that across both China and India millions of households are currently using POU devices to treat tap water of questionable quality. While the actual health benefits of each type of POU have yet to be definitively established, it is nonetheless clear that their efficacy in the field must be assured. In this context, the development of POU devices with integrated nanosensors that quantify performance should be encouraged.
Numerous low-cost (e.g., paper-based tests, lateral flow devices) and high-cost (e.g., electronic, cartridge based) sensor platforms have been described in the literature for water quality analyses\textsuperscript{11,15}. However, the transfer of such novel technologies from the laboratory to the marketplace is highly challenging with many pitfalls along the way\textsuperscript{34}. A key issue that must be considered at the outset is how to cover the costs associated with transitioning a laboratory device to the field. While the size and the competitiveness of the high-end POU market is arguably large enough to support the development, testing, deployment and marketing of new technologies\textsuperscript{37}, this is unlikely to be true at the lower-end of the POU market. As has been found for many promising low-cost point of care (POC) medical sensors, the challenges associated with transitioning novel diagnostic devices into either established markets or into new markets that target individuals at the ‘bottom of the pyramid’\textsuperscript{69} (i.e., the poor) are particularly vexing due to the lack of financial incentives critical for product development, testing, and marketing. In general, if new methods and new technologies are to gain a foothold then the potential profits associated with the new method must be high and the risks of adoption must be low.

Whether at the high-end or the low-end of the spectrum, the incorporation of nanosensors into POU devices or the development of stand-alone nanosensors will make it possible for consumers to test the quality of the water that they consume and to make conscious decisions as to whether it is of better quality than water from a bottle or other sources. In such a manner, water quality sensing will become increasingly democratized\textsuperscript{70} and as such consumers will gain knowledge that should spur improvements in water treatment and water potability.

\textbf{The Forward Path}
As noted previously, the water treatment field is conservative and novel analytical methods must either provide new capacity or be economically competitive relative to existing approaches if they are going to be ultimately useful. It is clear that great progress has been made in the development of nanomaterial-enabled sensors for medical and industrial application. The knowledge gained from these studies suggests the utility of such sensors within the water treatment arena. It must be recognized, however, that drinking water is a highly variable matrix that differs from the matrices (i.e., blood, plasma) in which many nanosensors have been developed and it is imperative that their utility in drinking water be fully established. Across the world, water quality can vary substantially due to differences in hardness, alkalinity (the capacity of a water to resist changes in pH), background macromolecular organic chemical content (e.g., natural organic matter), as well as inorganic and organic contaminants whose concentrations are highly dependent on the quality and type of source water used for drinking water production. Viable nano-enabled sensor platforms must have the capacity to detect analytes across this broad range of water quality conditions and in the possible presence of an oxidizing disinfectant. A wide variety of approaches are currently used to monitor water quality and detect contaminants. These approaches have been extensively tested and optimized over the course of many years. Given this fact, and the aforementioned conservative nature of the water treatment community, it is imperative that the sensitivity and specificity (i.e., method detection limits) of any nanosensor be evaluated across a range of water quality conditions and then explicitly compared to those obtained using the approaches the nanosensor is intended to replace.
When developing nanosensors the importance of material safety cannot be considered at the end of the design cycle, but instead should be a key part of the initial design. A great body of literature has evaluated the health and environmental implications of nanomaterials and that literature should be drawn upon to evaluate appropriate materials for nanosensor design\textsuperscript{71,72}. The Principles of Green Chemistry as applied to nanotechnology provide a useful framework that ideally can be used to develop appropriate, sustainable, and nontoxic designs that still elicit the desired functionality\textsuperscript{73}.

The potential for nanosensors to address water contamination both in the more-highly and the less-highly developed parts of the world can only be reached through continual improvements in sensor design and the rigorous testing of different designs under realistic conditions. Nanosensors promise device miniaturization and the capacity for multiplex detection across contaminant classes. Achievement of these goals will help our global society collectively address the issue of equitable access to knowledge about the safety of the water that each of us consumes. The potential for nanotechnology enabled sensors for water quality monitoring is great, but for now remains just a hopeful promise.

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**Competing Interests.** The author declares no competing financial interests.
Figure 1. Representative optical, electrical, magnetic, and mechanical nanosensor platforms. A) Surface enhanced Raman (SERS) based detection of magnetically separated bacteria. In this assay, a sample containing bacteria of interest is treated with gold coated magnetic core nanoparticles functionalized with bacterium specific antibodies (MnFe$_3$O$_4$@Au-antibody). The nanoprobe/bacteria aggregate is magnetically isolated, amended with antibody functionalized gold nanorods (AuNR-antibody) and then probed by SERS. Reproduced from Ref.$^{118}$ with permission from The American Chemical Society; B) Preparation and use of a gold-reduced graphene oxide (rGO) nanocomposite based biosensor and its application for the electrochemical detection of organophosphorus pesticides (OP). A glassy carbon electrode (GCE) was functionalized via treatment with rGO, electropolymerization of pyrrole, electrodeposition of gold, and the co-deposition of silica and acetylcholinesterase (AChE). In the presence of an OP the electrical current is reduced relative to its absence. Reproduced from Ref.$^{119}$ with permission from The Royal Society of Chemistry; C) Combined magneto-fluorescence approach for detection of bacteria using fluorophore labeled magnetic nanoparticles. Magneto-fluorescent nanosensors (MFnS) functionalized with *E. coli* specific antibodies provide the capacity for fluorescence and magnetic bacterial detection. Reproduced from Ref.$^{117}$ with permission from The American Chemical Society.

Figure 2. Internet of Things (IoT) enabled water sensing both within the distribution system as well as at selected points within premise plumbing. At each sensor node a suite of nanosensors can be deployed for water quality monitoring.
### Table 1. Regulated drinking water contaminants – U.S. and E.U.

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<tbody>
<tr>
<td><strong>Microorganisms</strong></td>
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<tr>
<td>Cryptosporidium</td>
<td>Treatment technique (TT)[^5]</td>
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<td>Total coliforms</td>
<td>&lt;5% of samples positive</td>
<td>0/100 mL</td>
<td>Y (for E. coli)</td>
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<tr>
<td>+fecal coliforms or E. coli[^1]</td>
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<td><strong>Inorganic Chemicals</strong></td>
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<td>Antimony (Sb)</td>
<td>6 µg/L</td>
<td>5.0 µg/L</td>
<td>Y</td>
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<tr>
<td>Arsenic (As)</td>
<td>10 µg/L</td>
<td>10 µg/L</td>
<td>Y</td>
</tr>
<tr>
<td>Asbestos</td>
<td>7 × 10[^6] fibers/L</td>
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<td>N</td>
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<td>Barium (Ba)</td>
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<td>Beryllium (Be)</td>
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<td>N</td>
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<td>Boron (B)</td>
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<td>N</td>
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<td>Cadmium (Cd)</td>
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<td>5 µg/L</td>
<td>Y</td>
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<td>Chromium (Cr)</td>
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<td>50 µg/L</td>
<td>Y</td>
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<td>Cyanide (CN)</td>
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</tr>
<tr>
<td>Fluoride (F)</td>
<td>4000 µg/L</td>
<td>1500 µg/L</td>
<td>Y</td>
</tr>
<tr>
<td>Lead (Pb)</td>
<td>TT[^5]; Action level = 15.0 µg/L</td>
<td>10 µg/L</td>
<td>Y</td>
</tr>
<tr>
<td>Mercury (Hg)</td>
<td>2 µg/L</td>
<td>1 µg/L</td>
<td>Y</td>
</tr>
<tr>
<td>Nickel (Ni)</td>
<td>20 µg/L</td>
<td>N.A.</td>
<td>N</td>
</tr>
<tr>
<td>Nitrate (NO[^3]_)</td>
<td>10,000 µg/L (as N)</td>
<td>50,000 µg NO[^3]_/L</td>
<td>Y</td>
</tr>
<tr>
<td>Nitrite (NO[^2]_O)</td>
<td>1,000 µg/L (as N)</td>
<td>500 µg NO[^2]_O/ L</td>
<td>Y</td>
</tr>
<tr>
<td>Selenium (Se)</td>
<td>50 µg/L</td>
<td>10 µg/L</td>
<td>Y</td>
</tr>
<tr>
<td>Thallium (Th)</td>
<td>2 µg/L</td>
<td>N.A.</td>
<td>Y</td>
</tr>
<tr>
<td><strong>Organic Chemicals</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Acrylamide, Alachlor, Atrazine, Benzene, Benzo(a)pyrene, Carbofuran, Carbon tetrachloride, Chlordane, Chlorobenzene, 2,4-D, Dalapon, 1,2-dibromo-3-chloropropene, o-dichlorobenzene, p- dichlorobenzene, 1,2-dichloroethane, 2,2-dichloroethane, 1,1- dichloroethene, cis-1,2-dichloroethene, trans-1,2-dichloroethene, dichloromethane, 1,2-dichloropropane, Di(2-ethylhexyl) adipate, Di(2-ethylhexyl) phthalate, Dinoseb, Dioxin (2,3,7,8-TCDD), Diquat, Endothall, Endrin, Epichlorohydrin, Ethylbenzene, Ethylene dibromide, Glyphosate, Heptachlor, Heptachlor epoxide, Hexachlorobenzene, Hexachlorocyclopentadiene, Lindane, Methoxychlor, Oxydem (Vydaste), Polychlorinated biphenyls (PCBs), Pentachlorophenol, Picloram, Simazine, Styrene, Tetrachloroethylene, Toluene, Toxaphene, 2,4,5-TP (Silvex), 1,2,4-Trichlorobenzene, 1,1,1-Trichloroethane, 1,1,2-Trichloroethane, Trichloroethylene, Vinyl chloride, Xylenes (total)</td>
<td>Varies depending on the contaminant</td>
<td>Varies depending on the contaminant</td>
<td>Y or N (contaminant specific)</td>
</tr>
<tr>
<td><strong>Disinfection By-Products</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Bromate (BrO[^3]_)</td>
<td>10 µg/L</td>
<td>10 µg/L</td>
<td>Y</td>
</tr>
<tr>
<td>Chlorite (ClO[^2]_)</td>
<td>1000 µg/L</td>
<td>N.A.</td>
<td>N</td>
</tr>
<tr>
<td>Haloacetic acids (HAAs)[^3]</td>
<td>60 µg/L</td>
<td>N.A.</td>
<td>Some HAAs</td>
</tr>
<tr>
<td>Trihalomethanes (THMs)[^4]</td>
<td>80 µg/L</td>
<td>100 µg/L</td>
<td>Some THMs</td>
</tr>
</tbody>
</table>

[^1]: Total coliforms are bacteria that are naturally present in the environment. Fecal coliforms are a subset that only come from human and animal fecal waste. Fecal coliforms are used as indicator organisms to indicate that water may be contaminated by fecal waste.

[^2]: Enteric viruses (enteroviruses) inhabit the intestines of infected humans and animals. The group includes polioviruses, coxsackieviruses, echoviruses, and others.

[^3]: Five regulated haloacetic acids: dichloroacetic acid, trichloroacetic acid, chloroacetic acid, bromoacetic acid, and dibromoacetic acid. The total mass concentration is regulated.

[^4]: Four regulated trihalomethanes: bromodichloromethane, bromof orm, dibromochloromethane, and chloroform. The total mass concentration is regulated.

[^5]: Treatment technique (TT). These contaminants are regulated based upon a minimum required set of treatment techniques that are expected to result in sufficient contaminant removal to protect public health.

[^6]: Evaluated using a Google Search of the terms ['nanosensor' and 'contaminant_name']
<table>
<thead>
<tr>
<th>Sensing Strategy</th>
<th>Nanomaterial types</th>
<th>Analytes</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Optical</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Colorimetric</td>
<td>Gold nanoparticles, Silver nanoparticles</td>
<td>NO₂⁻, NO₃⁻, cocaine, Pb²⁺, Cu²⁺, Hg²⁺</td>
<td>74-78</td>
</tr>
<tr>
<td>Fluorescence</td>
<td>Quantum dots</td>
<td>Heavy metals (Cd²⁺, Pb²⁺, Hg²⁺, Cu²⁺)</td>
<td>79-90</td>
</tr>
<tr>
<td>Surface-enhanced Raman (SERS)</td>
<td>Gold nanoparticles</td>
<td>Pesticides, bacteria, viruses, protozoa</td>
<td>83-86</td>
</tr>
<tr>
<td><strong>Electrical</strong></td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>Chemiresistors</td>
<td>Gold nanowires</td>
<td>halides</td>
<td>97</td>
</tr>
<tr>
<td>Metal oxide semiconductor nanowires</td>
<td></td>
<td>Volatile organic compounds (VOCs), NO₂</td>
<td>98-100</td>
</tr>
<tr>
<td>Polymer nanowires</td>
<td>Fe³⁺, VOCs, Ammonia</td>
<td></td>
<td>101-103</td>
</tr>
<tr>
<td>Field-effect transistors (FETs)</td>
<td>Silicon Nanowires (SiNWs)</td>
<td>Nucleic acids, influenza</td>
<td>104,105</td>
</tr>
<tr>
<td>2D transition metal dichalcogenides (MoS₂, WSe₂, MoTe₂, etc...)</td>
<td>Glucose, H₂O₂, proteins, Hg³⁺, pH</td>
<td>106,107</td>
<td></td>
</tr>
<tr>
<td>Gold nanoparticle functionalized polymeric FETs</td>
<td>Hg³⁺</td>
<td>108</td>
<td></td>
</tr>
<tr>
<td>Phosphorene (black phosphorous)</td>
<td>IgG protein</td>
<td></td>
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<tr>
<td><strong>Electrochemical</strong></td>
<td>Graphene</td>
<td>Bacteria</td>
<td>109</td>
</tr>
<tr>
<td>Carbon nanotubes</td>
<td>Ammonium, Co³⁺ organo-phosphate pesticides</td>
<td>110-112</td>
<td></td>
</tr>
<tr>
<td>Copper nanowire electrodes</td>
<td>Nitrate</td>
<td></td>
<td>113</td>
</tr>
<tr>
<td>Polymeric nanocomposite membranes</td>
<td>Ag³⁺, Hg³⁺, Cu³⁺</td>
<td></td>
<td>114</td>
</tr>
<tr>
<td>Reduced graphene oxide/gold nanoparticle nanocomposite</td>
<td>Organo-phosphate pesticides</td>
<td></td>
<td>115</td>
</tr>
<tr>
<td><strong>Magnetic</strong></td>
<td></td>
<td></td>
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</tr>
<tr>
<td>Magnetoresistance</td>
<td>Magnetite (Fe₃O₄); maghemite (γ-Fe₂O₃)</td>
<td>Mycobacterium bovis; Influenza A</td>
<td>30,31,116</td>
</tr>
<tr>
<td>Hydrodynamic property changes</td>
<td>Magnetite (Fe₃O₄)</td>
<td>Spore detection</td>
<td>52</td>
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<tr>
<td>T₂ relaxation magnetic resonance</td>
<td>Magnetic beads</td>
<td>Salmonella enterica and Newcastle disease virus (as a representative virus); E coli 0157:H7</td>
<td>33,117</td>
</tr>
</tbody>
</table>