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Irrigation Water Quality—A Contemporary Perspective

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Review

Irrigation Water Quality—A Contemporary Perspective

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Abstract: In the race to enhance agricultural productivity, irrigation will become more dependent on poorly characterized and virtually unmonitored sources of water. Increased use of irrigation water has led to impaired water and soil quality in many areas. Historically, soil salinization and reduced crop productivity have been the primary focus of irrigation water quality. Recently, there is increasing evidence for the occurrence of geogenic contaminants in water. The appearance of trace elements and an increase in the use of wastewater has highlighted the vulnerability and complexities of the composition of irrigation water and its role in ensuring proper crop growth, and long-term food quality. Analytical capabilities of measuring vanishingly small concentrations of biologically-active organic contaminants, including steroid hormones, plasticizers, pharmaceuticals, and personal care products, in a variety of irrigation water sources provide the means to evaluate uptake and occurrence in crops but do not resolve questions related to food safety or human health effects. Natural and synthetic nanoparticles are now known to occur in many water sources, potentially altering plant growth and food standard. The rapidly changing quality of irrigation water urgently needs closer attention to understand and predict long-term effects on soils and food crops in an increasingly fresh-water stressed world.

Keywords: crop uptake; food quality; geogenic; emerging contaminants; nanomaterials

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1. Introduction

Irrigation is the controlled use of multiple water sources in a timely manner for increased or sustained crop production. Irrigation comprises of the water that is applied by an irrigation system during the growing season and also includes water applied during field preparation, pre-irrigation, weed control, harvesting, and for leaching salts from the root zone [1]. In 2015 it was estimated that in the United States irrigation alone accounted for 62% of water usage [1]. Globally, irrigation is the highest consumptive use of freshwater [2]. As the world's population grows, the risk increases that more people will be deprived of adequate food supplies in impoverished areas, particularly those subject to water scarcity [3]. Agricultural production of food needs to increase by an estimated 60% by 2050 to ensure global food security [3] and irrigation will increasingly be called upon to help meet this demand. In the race to enhance agricultural productivity, irrigation will become even more dependent on substandard sources of water. Therefore, it is of utmost importance to access our current state of knowledge and explore the effects of irrigation water quality on crops. This understanding will help ensure adequate crop production to meet increased demand as well as to maintain proper food and soil quality.

Groundwater exploitation (withdrawal for irrigation) can release naturally occurring geogenic contaminants, such as arsenic, from the solid phase to groundwater, while wastewater reuse can concentrate pesticides, pharmaceuticals and other emerging contaminants in irrigation water [4,5]. Use of untreated wastewater is becoming prevalent in developing countries where around 80–90% of wastewater remains untreated [6]. Polluted municipal, industrial or agricultural water used for irrigation significantly changes soil quality, increases the amount of trace elements in soil and plants, and acts as a source of various pathogens which affects food quality and safety [7,8]. Water of inadequate quality is a potential source of both direct and indirect contamination to food crops [9], and leads to increased contamination of soil and water [10,11]. In addition, the presence of synthetic and natural nanomaterials is beginning to be identified in crops [12–14]. In locations where excess irrigation is practiced, contaminants in soils are leached to the vadose zone, where they can contribute to geogenic contaminant mobilization and potentially increase contaminant levels in local groundwater [15]. Many aspects of water composition, such as hardness and iron content, also affect the suitability of a water source for newer, more efficient spray or drip irrigation techniques. Runoff, return flow, and leaching of irrigation water also contribute to local surface and groundwater contamination [16]. Increased usage of irrigation water has already led to impaired irrigation water and soil quality. Considering the presence of new contaminant types in different water sources (see Figure 1), it is essential to evaluate the impact of these contaminants within the context of modern agriculture. To date, very little research and regulatory attention has been paid to contaminants in irrigation water. Contamination of irrigation water supplies is likely to worsen unless additional efforts (research, guidelines, regulations, treatment methods) are brought to bear on this problem.

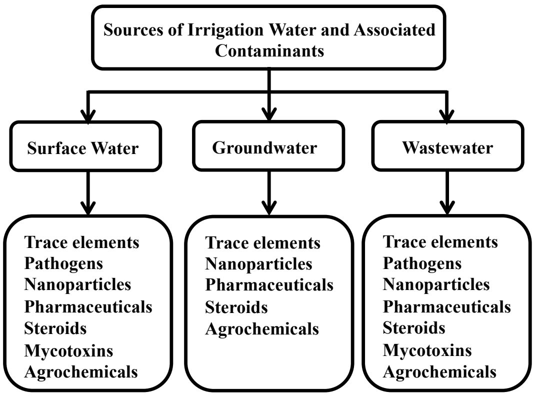

Figure 1. Main sources of irrigation water and different types of contaminants present in those sources impacting food, soil, and water quality. Note that surface water and wastewater are subject to similar types of contamination.

This review article looks at previous approaches to define irrigation water quality and compares to a current perspective with respect to impacts on human health. It evaluates the long-term effect and influence of the changing quality of water sources used in agricultural production. Although the article discusses traditional irrigation water quality concerns, such as salinization, it mainly emphasizes contemporary water quality issues like new or emerging contaminants, pathogens, geogenic trace elements and engineered nanomaterials. These contaminants are now widespread in various conventional and unconventional water sources used for modern-day irrigation. The article is organized as a short summary of conventional measures of irrigation water quality followed by a more detailed evaluation of the impact of contemporary irrigation water quality issues on soil and crop quality. Contemporary topics include emerging contaminants with separate sections on pharmaceuticals, antibiotics, steroid hormones, pesticides, cyanotoxins and mycotoxins, biological contaminants bacteria, virus and antibiotic resistance genes, modern inorganic contaminants, such as geogenic trace elements and nanomaterials. The review is summarized by considering the changing quality of water sources used for irrigation, and the need for additional work and improved regulation of irrigation water, especially for food production. The primary focus of this review is to recognize water quality issues that have a direct or indirect influence on surface soil contamination, crop uptake of contaminants and their potential to impact human health. This article shows a need for modern guidelines, regulations and research to understand the complex nature of irrigation water. Though it is a critically important topic from a human health standpoint, this review does not include an exhaustive discussion of contamination of irrigation water by human pathogens. While wastewater treatment technologies are constantly evolving and can address some of the issues presented here, a review of wastewater quality as a function of treatment technology is beyond the scope of this article. Moreover, treatment approaches are likely to be tailored to sources, and irrigation water sources are highly varied depending on climate, population, industry, crop, and livestock density.

2. Conventional Measures of Irrigation Water Quality

The effect of irrigation water composition on soil properties for crop production has been a focus for the past half century. Previous studies of water quality issues, and the suitability of freshwater sources for irrigation, have primarily been directed toward an understanding of potential problems to soil salinity, fertility and crop growth. For example, early work by the United States Geological Survey (USGS) [17] evaluated groundwater quality in Texas for irrigation and other potentially competing uses. A subsequent report by Schwennesen and Forbes characterized groundwater in San Simon Valley, Arizona and New Mexico, for domestic use and irrigation [18]. Clark reported on the chemical composition of groundwater in the Morgan Hill area of California [19], while Scofield and Headly [20] evaluated water composition with respect to irrigation potential. Most of these early works focused on understanding the impact of water quality on long-term viability of irrigation in arid regions of the United States.

Globally, irrigation water quality was described in Tanzania, Africa, with respect to pH and alkaline and alkaline-earth elements [21]. Taylor et al. reported that irrigation water pH was one of the main factors for wheat growth in Punjab, India [22]. A subsequent work reiterated that alkaline elements such as sodium play a crucial role in continued use of water for irrigation of cropland and quantified the maximum amount that may be tolerated [23]. The effects of soil salinization and trace element composition on crop growth have become more apparent over time. Eaton et al. reported that boron present in water around Hollister, California affected the growth of apricots and prunes [24]. In the subsequent years, the United States Department of Agriculture (USDA) conducted further studies and reported that sodium, boron and electrical conductivity are the best general measures for judging the suitability of water for irrigation [25]. From these studies, it was evident that continuous irrigation with water of marginal quality impacted soil and also affected crop growth [26–31]. In 1967, the American Society for Testing Materials (ASTM) developed a quantitative assessment of irrigation water quality, including new formulas for maximum permissible quantity of chloride and electrical conductivity based on infiltration rate, evapotranspiration rate, irrigation frequency and duration [32]. Traditionally, discussion on irrigation water quality has mainly focused on its effect on soil quality, and how soil quality was predicted to affect crop growth and yield. Color, turbidity, total dissolved solids (TDS), pH, specific conductance, odor and foam characterized the quality of water. Colorless, odorless, foamless water with minimum turbidity, TDS below 1000 mg L^{-1} at circumneutral pH and specific conductance below 1.5 mmhos/m is generally considered to be of good quality for irrigation purposes [33,34]. A higher TDS is not recommended for most crops as it can impact the salinity of soil and pore water will become highly concentrated when taken up by roots via osmosis. Excessive dissolved solids content, or salinity of irrigation water, has historically been the primary characteristic determining water suitability for irrigation. Salt accumulation in the crop root zone impedes water uptake and can eventually prevent plant growth altogether [34]. Excess salinity from sodium can affect soil structure and water infiltration. The proportion of sodium to calcium and magnesium is the primary factor controlling the hydraulic conductivity of water in soil [33–35]. Sodium is generally expressed as a sodium absorption ratio (SAR) [9]. Long-term irrigation of soils with elevated sodium concentrations relative to calcium and magnesium, bicarbonate, carbonate, and TDS will be limiting soil aggregate formation, which reduces infiltration and makes less water available to crops [34].

Seiler et al., under the National Irrigation Water Quality Program (NIWQP) of the U.S. Department of the Interior (DOI), studied the effect of irrigation-induced contamination of water, soil and biota in the western United States. NIWQP data from the 26 areas under study suggested that degradation of groundwater quality due to irrigation is a common occurrence [11,36]. The study indicated that selenium was the most common contaminant, followed by arsenic, uranium and molybdenum [11,37]. This study also suggested regular co-occurrence of these contaminants. For example, selenium was found to be elevated with uranium, and these contaminants were accumulating in the soils and affecting long-term suitability for crop production. This was one of the first reports to correlate trace element contamination in water sources used for irrigation to soil quality. These findings led to the appreciation of the intricate complexities of irrigation water quality and its role in ensuring proper crop growth and long-term food quality. These studies mainly focused on the impact of water quality on crop productivity and soil quality, while effects to food quality and safety were just beginning to be recognized.

3. Impact of Contemporary Irrigation Water Quality Issues on Soil and Crop Quality

Irrigation water quality has mainly been characterized with respect to effects on crop growth and yield, though an emerging and pressing issue relates to plant uptake and soil enrichment with inorganic and organic contaminants (Figure 2). These "new" issues with respect to irrigation water quality can lead to food quality and safety concerns, as well as affect crop growth and yield [38–41]. Wastewater reuse for irrigation contributes to increasing incidence of organic microcontaminants [42], such as pharmaceuticals and other synthetic organics in soils and crops. Increasing reliance on groundwater also contributes to the probability for elevated concentrations of natural geogenic contaminants such as arsenic and selenium in irrigation water and soils. Understanding the occurrence and fate of these new contaminants in irrigation water sources is paramount in limiting the effects to modern agricultural products [43]. Long term impacts to soil and crop quality (see Figure 2) need to be understood.

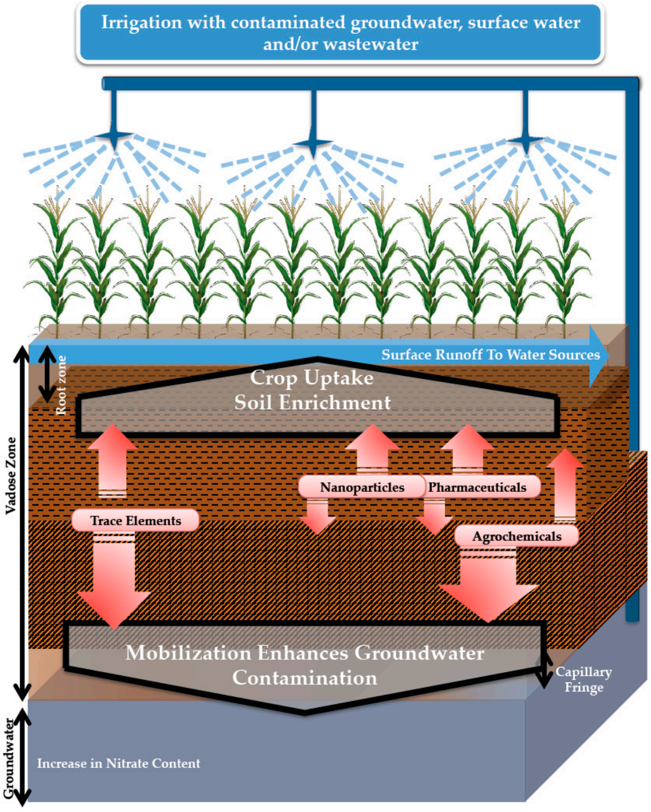

Figure 2. A conceptual model of the impact of inadequate quality of irrigation water sources on soil and crop quality.

3.1. Emerging Contaminants: Organic Pollutants

3.1.1. Pharmaceuticals

Traces of pharmaceuticals and personal care products have been identified in a variety of freshwater sources, including drinking water [44], groundwater [45], and surface water [45]. Pharmaceuticals can enter the water system from various sources, including direct disposal and human excretion into sewers leading to elevated concentrations of pharmaceuticals in wastewater [46]. Pharmaceuticals often detected in sewage sludge include non-steroidal anti-inflammatory drugs (NSAIDs), blood thinners, psychiatric drugs, antidiuretics and β-blockers [47–49]. Plant uptake of a wide variety of pharmaceutical groups like NSAIDs, antihistamine, β-blockers, calcium channel blockers, antiepileptics, steroid hormones, antidepressants, antineoplastic agents, anti-itch compounds, x-ray contrast agents, lipid-lowering agents, benzodiazepines, tranquilizers and veterinary drugs from soil and contaminated water has been observed and studied [50–52]. Wu et al. reported that a primary pathway for contamination by pharmaceuticals in food crops is through irrigation water [53,54]. For example, a recent study found traces of carbamazepine, caffeine, lamotrigine, gabapentin and acesulfame in a variety of vegetables grown with treated wastewater in Jordan [55]. Treated wastewater is well known to contain a large variety of pharmaceuticals and personal care products, many of which are known to accumulate in food crops [56,57]. The occurrence of these and other synthetic organic chemicals is likely to increase in water supplies, especially in areas with water scarcity, and irrigation with contaminated water will lead to soil contamination and plant uptake.

3.1.2. Antibiotics

Environmental contamination by antibiotic residues in food production systems is a growing problem worldwide, and the potential implications to proliferation of antibiotic resistance have been the subject of multiple reviews and opinion articles [58–60]. The occurrence of persistent antibiotic residues in various water sources [61,62] is well documented which not only includes municipal [63,64], agricultural [65,66] and hospital sewage [67,68] but also groundwater [69] and surface water [70–72]. The concentration range of antibiotics is generally measured at ng L^{-1} to a few μg L^{-1} in many water sources [73], though concentrated wastewater can have much higher levels [65]. Recent studies have demonstrated that plants can take up antibiotics (like amoxicillin, ketoconazole, lincomycin, oxytetracycline, sulfamethoxazole, sulfonamides, and tetracyclines) [74–76] and antibiotic contaminated irrigation water can play a significant role in the uptake [77]. The environmental fate and transport of antibiotics depend on various physical properties such as water solubility, lipophilicity, volatility and sorption potential [77].

The implications to human health due to the presence of antibiotics in food crops is not clear, but other potential adverse impacts include allergic reactions, disruption of digestive function and chronic toxic effects as a result of prolonged low-level exposure [78–81]. One of the major concerns for the increasing prevalence of antibiotics in the environment is the development and spread of antibiotic-resistant gene and bacteria [82], which is discussed in Section 3.2.2. Clearly, the absence of antibiotic residues in irrigation water cannot be assumed.

3.1.3. Steroids

Land application of livestock manure can contribute to accumulation of steroid hormones [83] and veterinary pharmaceuticals. Very low concentrations of natural steroid hormones, such as estrone, 17α-estradiol, 17β-estradiol, estriol, testosterone, androstenedione and progesterone that occur in animal waste and wastewater have been documented as accumulating in soil [84]. Traces of steroid hormones have also been reported in groundwater [85] and surface water [86], and often in treated municipal wastewater [87–91]. Wastewater treatment plants are known to discharge these hormones into river water and also other recipients [92]. Laboratory experiments have suggested that traces of steroid hormones and pharmaceuticals can be taken up in crops [93] and recent studies of food crops irrigated with treated municipal water have confirmed this can occur in the field. Further work is needed to understand the significance and impact of these chemicals in the environment and to human health [94], though at present, the reported concentrations are relatively low in comparison to other contaminants.

3.1.4. Agrochemicals

Regular use of pesticides in irrigated crops is also likely to lead to the occurrence of these residues in irrigation water and food crops, especially in regions where regulation and training in proper application of these substances is lacking. Application of large quantities of agrichemicals and improper management can create a substantial effect on the environment. The leaching and runoff of agrochemicals is a potential source of groundwater and surface water contamination [95,96]. The occurrence of agrichemical residues in vegetables has been documented [97] and their uptake by crops is well studied [98,99] and regulated. Leaching of nitrate from fertilizer over application to groundwater below is well reported, and accumulation of reactive nitrogen is also thought to initiate mobilization of other geogenic contaminants [15].

3.1.5. Cyanotoxins and Mycotoxins

Cyanotoxins, which comprise a large range of naturally produced organic compounds, are produced and released by cyanobacteria when they are present in large quantities (blooms) and especially when these organisms die off and decay in surface water. Cyanobacteria also referred to as blue-green algae, naturally occur in all freshwater ecosystems [100]. Warmer temperatures coupled with high nutrient concentrations are thought to favor conditions for algae blooms to form in surface water. Of many different groups of cyanotoxins, hepatoxic cyclic peptides collectively known as microcystins are the most commonly studied cyanotoxins, which cause a wide range of symptoms in humans [101]. Other studies have also shown that cyanotoxins, which include hepatotoxic microcystins and neurotoxic compounds such as anatoxin-a and beta-*N*-methylamino-alanine, can make their way to human and animal food chain from contaminated reservoirs [102–105]. A recent review has summarized the extent of the literature investigating the fate in soils, and agricultural crops [103]. It seems quite clear that toxins can accumulate in plants, including food crops and under some conditions can also inhibit plant growth [102,103,106–108]. Though there are many gaps, and only a handful of studies have investigated this route for exposure. There is evidence for human health effects through consumption of plants contaminated with cyanotoxins by irrigation using surface water sources impacted by cyanotoxins.

Mycotoxins are naturally occurring fungal toxins (chemicals), which can cause a variety of adverse health effects to both humans and livestock. A few mycotoxins are known or suspected carcinogens. Fungi do pose potential hazards to human health. However, there were relatively few studies of mycotoxins in water sources until recently. Fungal contamination has been observed in drinking water [109] and recently it was reported that untreated surface water can be breeding place for these fungi, generating mycotoxins [110]. Kolpin et al. led a broad scale study on the occurrence of mycotoxins across streams in the United States (US) [111]. Their study concluded that the ecotoxicological effects from long-term, low-level exposures to mycotoxins are poorly understood and would require further investigation. Mycotoxin uptake in rice has been studied [112] and these chemicals have been reported to be present in various food grains [113,114]. The prevalence of mycotoxins in surface water makes it an important consideration regarding modern water quality of irrigation as mycotoxin health hazards are widely reported.

3.2. Biological Contaminants: Bacteria, Virus and Antibiotic Resistance

3.2.1. Pathogens

Often because of its nutrient content and accessibility, untreated wastewater from municipal and domestic sources containing excessive levels of pathogens is often directly used for irrigation in developing countries [6]. Untreated wastewater generally carries a high pathogen load compared to other irrigation water sources. Risks from pathogen (bacteria, viruses, or protozoan or larger organisms) contamination to irrigation water quality will continue to be a topic of primary concern [115–117], and it is impossible to adequately address this topic in a few paragraphs. Pathogenic microorganisms in irrigation water likely pose the greatest acute risk to human health and will continue to be a concern especially in freshly-eaten produce. Pathogens are biological organisms that may influence modern-day irrigation water quality. Pathogen contamination is generally related to surface water sources, but groundwater may also be under threat if it is recharged with wastewater sources [116]. The complexity of reproducibly measuring microbiological contamination of irrigation water has made monitoring difficult. Several different types of pathogens have been detected in diverse irrigation water sources including bacteria (e.g., *Salmonella* and *Escherichia coli*), protozoa (e.g., *Cryptosporidium* and *Giardia*), as well as viruses (e.g., noroviruses)) [118,119]. Irrigation of food crops with surface water clearly has the highest potential for contaminating freshly eaten produce, and this topic has had the greatest research and regulatory effort in recent years.

There have been quite a few comprehensive reviews emphasizing irrigation water as a source of pathogenic microorganisms in fresh produce [120–123]. Between 1973 and 2012, the Centers for Disease Control and Prevention reported 606 leafy-vegetable associated pathogenic outbreaks (norovirus (55% of outbreaks), Shiga toxin-producing *Escherichia coli* (STEC) (18%), and *Salmonella* (11%)), with 20,003 associated illness and 19 deaths [124]. From 2013 to 2017, the number of outbreaks (mainly from norovirus (32%) STEC (23%), and *Salmonella* (32%)) associated with leafy greens and vegetables decreased to 21, with 699 illness and five deaths [125]. In 2018, 272 infections were reported from two outbreaks (*E. Coli*) associated with romaine lettuce resulting in five deaths [126,127], and another multi-state outbreak was linked to parasite *Cyclospora*, which reported 511 cases of infection [128]. However, a 2014 risk-based review conducted in California suggests that recycled water quality criteria, along with proper agricultural management practices do not lead to increased public health risk [129]. In the US, the Center for Produce Safety has published information on the factors that affect the microbiological safety of agricultural water [130]. The Foodborne Disease Outbreak Surveillance System (FDOSS) has an online tool, the National Outbreak Report System (NORS), which keeps track of outbreaks in the United States. Reports of pathogen contamination from inadequately treated wastewater have also been documented in developing countries [8]. The occurrence of pathogens in water used to irrigate food crops is considered a severe problem affecting human health both in both developing and even in developed countries [131]. Groundwater sources are generally considered less vulnerable to contamination by pathogenic microorganisms, while surface water and wastewater have a much higher potential for contamination. Farmers utilizing surface water for food crops, which are consumed raw should follow proper mitigation strategies to control contamination [132]. The method utilized for irrigation has a substantive role in pathogenic contamination of crops. For example, subsurface drip may have the lowest risk as the water is generally applied at the root zone, unlike other methods (e.g., sprinkler irrigation) where the edible portions of crops can come in contact with contaminated water [133]. New and more intensive monitoring approaches and potential disinfection and treatment techniques for surface water used to irrigate food crops are needed to improve food safety [8].

3.2.2. Antibiotic Resistance

The World Health Organization (WHO) has listed antibiotic resistance among today's biggest threats for global health, food safety, and development, as this threatens the ability to treat common infectious diseases [134]. Antibiotic resistome is defined as the sum of all genes directly or indirectly contributing to antibiotic resistance both in the clinics and the environment [135]. Aquatic ecosystems are regarded as a primary reservoir of antibiotic-resistant bacteria (ARB) [136]. The presence of ARB and their resistance determinants in surface water sources have been well documented and is generally linked to nearby wastewater treatment plant effluent [137–141]. Wastewater treatment plants enrich ARB and their resistance determinants as it favors exchange of antibiotic resistance genes (ARG) among bacteria and selection of resistant strains [142]. In a recent study, it was found that multidrug-resistant (MDR) bacteria were found to be more prevalent in surface waters than in treated wastewater [143].

Irrigation water is one of the major sources for contamination of fresh produce with antibiotic resistance bacteria [58,144,145]. Similar to pathogens, the incidence of ARB contamination is higher when using overhead sprinklers as water can directly come in contact with fresh produce. When fresh produce is consumed raw it can act as an ideal vector for exposure. The diversity of ARB present in fresh produce is significant and can have a severe impact on human health.

3.3. Inorganic Contaminants: Geogenic Source and Nanomaterials

3.3.1. Geogenic Contaminants in Irrigation Water

Selected naturally occurring geogenic contaminants, such as boron, arsenic and selenium, have been the subject of much previous work focused on irrigation water quality [146,147], especially in areas with extensive use of groundwater. With the exception of boron, trace element contaminants were not studied with respect to soil quality, crop productivity and phytotoxicity [9]. Boron is an essential trace element for plant growth, but elevated boron concentrations (>1 mg/L) in irrigation water can cause stunted growth and reduced productivity in sensitive crops such as wheat. The occurrence of geogenic contaminants is a growing contemporary issue because of the potential impact on food quality and human health. Concentrations of geogenic contaminants have likely been increasing over time in a variety of irrigation water sources, often due to increasing agricultural intensification [148,149]. Researchers have reported that groundwater in China has elevated levels of arsenic; this water is used for irrigating feed crops [150]. Similarly, studies in the United States have reported higher levels of uranium [15] and arsenic [151] in its aquifers. India, Bangladesh and Vietnam have widespread arsenic contamination in groundwater used for drinking and irrigation, especially in areas where the use of contaminated water has led to contaminated soils and crops [152–154]. Presently there are no federal guidelines regulating geogenic contaminant levels in irrigation water except in the case of direct wastewater reuse [155,156]. The increasing levels of contaminants in soils and irrigation water are a growing issue across the globe, and there is little work to date regarding strategies to mitigate accumulation in plants and food crops. Contaminant uptake by crops has been well studied and plant uptake has even been used as a remediation method, viz. phytoremediation. However, mitigation strategies for prevention of geogenic contaminant uptake by plants have received scant attention in the literature. Plant uptake and accumulation of specific trace elements may not affect plant growth, but accumulation and consumption may pose hazards to animal or humans.

Table 1 summarizes the estimated ranges of aqueous concentrations of many geogenic elements with respect to guidelines and recommendations of water use. Irrigation water guidelines compiled by the Food and Agriculture Organization (FAO) in 1976 are generally based on the toxic effects to crops and plant growth [157]. FAO has recommended using these values as guidelines for irrigation utilizing groundwater and surface water sources, but not for irrigation with wastewater containing measurable levels of trace elements [157]. Wastewater guidelines set by FAO (Table 1) are equivalent to irrigation water quality recommendations in 1976, though may contradict newer guidelines for special constituents of wastewater [157]. Early recommendations rarely consider uptake of trace elements by crops and the impact on food quality, which may affect human health. Recommended concentrations to ensure consistent food quality are absent, as even low concentrations of geogenic contaminants can impact food quality (Table 1) [158–172]. Continuous use of irrigation water with low concentrations of geogenic contaminants concentrations can result in soil enrichment and affect food crop quality [158–172].

Table 1. Common geogenic trace element contaminants in irrigation water with current regulatory and recommended levels (NA: Not Available, AL: Action level, CCC: Criterion continuous concentration, CMC: Criterion maximum concentration, SDWR: Secondary drinking water regulations). (* Few examples of plant uptake, ** in µg, *** greenhouse experiment concentration was equivalent to natural condition).

Trace Element	EPA Drinking Water Guideline (µg L^{-1}) [173]	Regulatory Limits for Wastewater (µg L^{-1}) [156,174,175]	Freshwater CCC, CMC Limits for Aquatic Life (µg L^{-1}) [176]	Recommended Maximum Concentrations of Trace Elements in Irrigation Waters (µg L^{-1}) [157]	Reported Ranges for Trace Elements in Glacier Aquifer System of USA (Includes Wells Used for Agriculture) (µg L^{-1}) [177]	Reported Ranges of Water Known to Impact Food and Soil Quality * (µg L^{-1})
Arsenic	10	100	340, 150	100	0.09–340	58.7 [158], 0.2–164 [159]
Boron	NA	NA	NA	1000	NA	3351–16,000 [165–167]
Cadmium	5	10	1.8, 0.72	10	0.018–1	<1–3200 [168]
Cobalt	NA	50	NA	50	0.007–95	0.21–0.81 [169]
Copper	1300 (AL)	200	NA	200	0.126–127	10–133 ** [170]
Chromium (III) or (VI)	100 (Cr)	100 (Cr)	570, 74 (III) 16, 11 (VI)	100 (Cr)	0.4–22 (Cr)	1–46 (VI) [171] ≤250 *** [172]
Iron	300 (SDWR)	5000	NA, 1000	5000	3–38,100	-
Lead	15 (AL)	5000	65, 2.5	5000	0.04–9.0	≤140 [160]
Lithium	NA	2500	NA	2500	0.040–126	-
Manganese	500 (SDWR)	200	NA	200	0.056–28,200	≤100 [160]
Nickel	-	200	470, 52	200	0.035–56	≤50 [160]
Selenium	50	20	NA	20	0.173–223	0.12–341 [161]
Silver	100 (SDWR)	NA	3.2, NA	NA	NA	-
Uranium	30	NA	NA	NA	0.009–162	1–1200 [162]
Zinc	5000 (SDWR)	2000	120, 120	2000	0.536–1000	~130 [168]

It is likely that irrigation with elevated levels of geogenic contaminants leads to contaminant enrichment in crops. For example, Bundschuh et al. [178] compiled data from different regions of South America known for high occurrences of arsenic in groundwater and surface water. Their study indicated that arsenic concentrations in edible plants and crops were associated with the elevated arsenic concentrations in soil and irrigation waters. The study showed that regions with high arsenic concentrations in surface water and groundwater relate directly to accumulation in plants, fish, livestock meat, milk, and milk products. Their study indicates that there is a need for more rigorous studies in evaluating pathways of arsenic exposure through the food chain in Latin America and other regions.

Factors such as arsenic speciation, type and composition of soil, and plant species also plays a significant role in crop uptake [179]. An interesting aspect of arsenic transformation is where arsenic present in soil may occur as oxidized arsenate (As(V)) but may become reduced to arsenite (As(III)) after uptake in crops [180]. Arsenite is regarded as 25–60 times more toxic to humans than arsenate [181]. Arsenic, by far, is the most studied geogenic contaminant in crops, especially rice, and is included in many review articles detailing its impact of food quality and human health [182–186]. Ongoing research is focused on managing arsenic uptake by crops [154,187,188]. Other geogenic contaminants in groundwater, such as uranium, are less well studied with respect to food contamination.

Elevated levels of selenium may be toxic, though selenium is an essential micronutrient for crops. Selenium is known to accumulate in crops grown on soils with high selenium content [161,189], and selenium enrichment has been reported in soils throughout the United States [190]. In their recent study, Wang et al. [191] found that volatile organic compounds released by plant growth-promoting rhizobacteria increases both selenium and iron uptake. Uranium is another geogenic, potentially toxic contaminant [192] and studies in nutrient culture show its uptake by crops [193,194]. Several studies confirmed that irrigation water contaminated with uranium has an impact on crop quality though less to soil contamination by uranium [195–197]. Lead, mercury [38], chromium [198] and cadmium [199] are also known to accumulate in crops grown on soils with high levels of these contaminants. While there is extensive information in the literature on uptake by plants, most studies have focused on the general type of contaminant, or its accumulation in crops, use in phytoremediation of soils and the pathway of uptake within the crop. Contaminated irrigation water is capable of enriching surface soil with these contaminants [200] and likely enhances availability for uptake by crops [197]. There are few federal guidelines for trace element limits in foods in the United States, other than in arsenic, lead, cadmium, and mercury in wastewater [201], and the evidence suggests there is an urgent need for irrigation water quality standards that include geogenic contaminants.

3.3.2. Engineered Nanomaterials

Earth is rich with natural nanomaterials and it is estimated that thousands of megatons move through the hydrosphere annually [14]. Natural nanoparticles in water can easily pass through conventional membrane filter pore sizes of 0.2-µm and may not be accounted for as nanoparticles [202], which adds to the complexity in understanding their impact on crop health. In the past decade, production and use of engineered nanoparticles have also risen significantly and continues to trend upwards. Nanoparticles are used in a wide variety of contemporary products, ranging from electronics and cosmetics to processed food. This proliferation in use of nanoparticles has paved their way to increasing occurrence in water sources [203,204]. Nanotechnology is also used widely for water treatment for both groundwater and surface water sources [205,206], but its repercussions are still not well understood [207]. In 2018, the occurrence of nanoparticle size plastics (nanoplastics) were critically reviewed with respect to human health and growing global occurrence in freshwater [208,209]. Analytical methods capable of detecting and quantifying nanoparticles in complex aqueous matrices are lacking, increasing the challenge in tracking fate and transport of these particles [207]. In 2005, Oberdörster et al. [210] reviewed the interaction of nanomaterials in regards to human health. Still, the full-scale toxicity of natural or engineered nanomaterials is not well understood in the context of complex biosystems [14]. The size of nanomaterials (100 nm or less in size) is the main factor [14] which makes studying nanoparticle contamination challenging. Therefore, the paradigm of risk assessment of nanoparticles needs to be reevaluated with respect to the unique challenges involved in monitoring environmental pathways and assessing impacts on human health.

Broadly, engineered nanoparticles can be classified into carbon and metal-based nanoparticles. Nanoparticles derived from carbon (e.g., carbon nanotubes) simultaneously act like particles and high molecular weight organic compounds. Metal oxides or metal nanoparticles must be evaluated for their metal-related chemotoxicity, and also toxicity arising due to their particulate form. These dual behaviors again add to the complexity of studying and assessing risk. Nanotoxicity can elicit significant effects to human health. Nanoparticles can be carcinogenic and may produce reactive species inside the body [211]. Ganguly et al. have recently reviewed the toxicity of nanomaterials, emphasizing major exposure pathways [211].

The nanoparticle life cycle is poorly understood. Therefore, the Environmental Protection Agency (EPA) has allowed limited manufacturing of new materials by administrative orders or new use rules under the Toxic Substances Control Act. These new rules have significantly expanded since their inception in 2010, which is on par with our increase in understanding. However, the use of and occurrence of nanomaterials in irrigation water is not monitored or regulated [206,212].

Nanotechnology usage is vital in modern civilization and will have a substantial impact on the world economy [213]. It is projected that the nanomaterials market will reach 55 billion US dollars by year 2022 [213]. Production of engineered nanoparticles is expected to rise in the coming years, making these contaminants more likely to occur in different water sources, both conventional (surface and/or groundwater) and in treated wastewater. Both carbon-based and metal-based nanoparticles are of concern and it has been reported these particles are persistent in water [214,215]. Nanomaterial transformation in fresh water systems is an active field of research [216]. Nanoparticle assessments have concluded that fine particulate matter occurs in a variety of water sources [217–221], so its impact on irrigation water, accumulation in soil, and potential for crop uptake is of paramount significance.

The growing availability of engineered nanomaterials/particles is relevant to understand how these nanosized particles may impact water and food quality in agriculture. The use of nanomaterials in agriculture is also increasing, and little data is available to understand how occurrence in irrigation water may influence crops [222,223]. There is recent work on uptake of both carbon and metal-based nanoparticles by plants. For example, multi-walled carbon nanotubes have been observed in broccoli, resulting in a positive impact on plant growth [224] but potentially creating health concerns. Carbon nanotubes are also known to act as a carrier for other contaminants (like organochlorine pesticide, etc.) in plants and enhance contaminant translocation [225]. These contrasting effects of carbon nanotubes have been well summarized in a recent review article by Vithanage et al. [226].

Metal oxide nanoparticles, which form a bulk of engineered nanomaterials, have been well studied under the purview of plant uptake [227]. Metal oxides like titanium dioxide, silver oxide, iron oxide, copper oxide and metal nanoparticles have been shown to accumulate in a variety of food crops and have even been detected in commercial produce [228–232]. A recent review by Ma et al. describes studies of nanoparticle uptake by crops and their occurrence in the final produce [40]. Similar to carbon-based nanoparticles, metal or metal oxide-based nanoparticles are also known to be beneficial to plant growth and have been marketed as nanofertilizers [233]. For example, iron oxide nanoparticles have shown to be a potential iron source for peanut crops [234]. Nanoparticles are also known to induce oxidative stress in crops [235]. A recent study by Liu et al. suggested that combinations of nanomaterials might have different impacts on the soil microcosm compared to a single nanomaterial [236]. In actual conditions, mixed nanomaterials will be more prevalent in soil and irrigation water. In addition to engineered nanomaterial, natural nanomaterials of silver are found in groundwater [237]. Life cycle assessment of engineered titanium dioxide nanoparticles showed that their impact is not just limited to crop uptake, but exhibit marine aquatic ecotoxicity and human toxicity [238,239]. Nanoscale is an important factor in ensuring uptake of fertilizer [240,241] but the long-term effects of nanoagrochemicals have yet to be studied [242]. While nanoagrochemicals may be beneficial to crops [243], they may have undesired effects on the environment and on human health [242].

There are many questions and few answers for understanding the effects of nanosized contaminants in irrigated agriculture. Future studies should be focused on understanding retention times and fate in water, plants and soils, including degradation and transformation rates, and biological effects of different forms. Naturally-formed nanoparticles can occur in irrigation water and in food crops and it is clear this route for exposure needs to be better understood and monitored. Are nanoparticles easily broken down in the environment or are they stable, do they form aggregates, and what is the accumulation in both soil and water sources? If they accumulate, how do they impact soil health and modern irrigation techniques? Nanoparticle occurrence and behavior in irrigation water sources, soils and plants is clearly an emerging area of research.

4. Changing Quality of Water Sources Used for Irrigation

This discussion on the changing composition and quality of different water sources for irrigation—be it conventional sources like surface- or groundwater, or nonconventional source like reclaimed water—signifies an urgent need for increased efforts to monitor the quality of agricultural water [244]. Recently, there have been various efforts to address changing water quality [9] by incorporating measurement of new contaminant types (e.g., arsenic, fluoride) [10,245,246] in water quality guidelines. Still, it is challenging to address the complexity of irrigation water quality covering different forms of geogenic and emerging contaminants. In the coming decades, the concentrations of specific contaminants will likely increase and continue to affect the quality of water sources for irrigation. Impending climate change may make the situation more extreme as drought and water scari]city may concentrate contaminants in water. The increasing prevalence of cyanotoxins may increase due to more intensive agriculture, fertilization and water use. Although there are strict guidelines for contaminant concentrations in drinking water, few guidelines exist for the use of water for any irrigation, including irrigation of food crops. The substantial expense of monitoring, including sampling and laboratory analysis, for "new" recently identified contaminants is a reason to implement a more practical approach for monitoring irrigation water quality, incomparison to the complex and expensive framework currently used for drinking water in developed countries.

Establishing regulations and clear guidelines for irrigation water quality in different countries or individual states of the United States for conventional sources of water is necessary, but not sufficient, to ensure healthy produce for human consumption. Proper food quality can only be insured if water sources are regulated and regularly tested. Testing can also be used to monitor accumulation of contaminants in soil. Moreover, plant tissue should also be checked periodically for contaminant uptake to ensure appropriate produce quality. Presently in the United States, reclaimed wastewater is regulated for irrigation usage [247,248] but almost any other source may be used without restriction. Guidelines are provided for pathogen levels in reclaimed wastewater [174]. There are recommendations for limits of geogenic contaminants in irrigation water in traditional sources [157,249] but there is a complete lack of recommendations or information on new and emerging organic contaminants or nanomaterials. There is a whole range of second and third generation nanomaterials proposed for commercial uses (e.g., nanocomposites and multi-element materials). These new nanomaterials will occur in waste streams and we have little understanding of their fate or toxicity. Moreover, the basis for existing recommendations is questionable, as concentrations far lower than some recommended values have been shown to be biomagnified in crops (see Table 1).

The present review focuses on the changing quality of water used for irrigation, and clearly there are many gaps to be addressed in future research. High priority should be given to research focused on improving our understanding and address the increasing occurrence of geogenic contaminants, pathogens and other biological contaminants in irrigation water, especially as they relate to food crops. Increased wastewater reuse for agricultural purposes will likely increase the occurrence of biologically active organic contaminants such as pharmaceuticals and antibiotics, and the effect on food crops and human health is also a major research gap. The dynamic nature of the chemical composition of different irrigation water makes it very important that relevant and periodic data is available for both conventional and nonconventional water sources. A more comprehensive set of water quality guidelines needs to be created incorporating our present understanding of the occurrence and effects of emerging contaminants. There should be specific recommendations for monitoring and tests at to check irrigation water quality used in agriculture. These recommendations can be soil specific, crop specific and water specific. The availability of new guidelines would help ensure better food quality, as the next generation will not only need larger quantities of irrigation water to feed the growing population, but health concerns may rise as we resort to the use of low-quality water to irrigate food and feed crops.

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