Assessment and Removal of Emerging Water Contaminants

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Abstract

This review summarizes recent literature related to analytical method development, assessment, and removal of emerging contaminants in natural water resources and drinking water. This review mainly focuses on the following four groups of chemical contaminants: pharmaceuticals and personal care products (PPCPs); major disinfection byproducts, cyanotoxins, and pesticides and herbicides. Because of the large volume publications on various emerging environmental contaminants, articles relating to specific water treatment, health risk assessments and ecological impact are not included in this review. In addition, literature pertinent to emerging contaminants in air and other environments are also not covered in this review.

Keywords: Emergency water contaminants; PPCPs; DBP; Cyanotoxins; LC-MS/MS; Pesticides and herbicides removal

Introduction

In recent years, because of the advanced analytical instrumentation and new analytical techniques, scientists have been able to detect very low concentrations of many chemicals in natural and drinking waters. These low levels of emerging contaminants in natural waters and drinking waters may not cause immediate lethal effect to humans but may promote disastrous impacts on human health in a long term. While the risk that low concentrations of emerging contaminants pose to humans and the environment requires further investigation, it is important to identify the concentrations of these compounds in natural and treated drinking waters so that effective techniques can be developed to remove these contaminants. Although no direct adverse impact on human health and ecological systems has been established from consuming drinking water that contains very low levels of some emerging contaminants, the potential for their long term accumulative effect on human health has caused a public concern.

To address the emerging contaminant issues, many university research laboratories, federal agencies such as the Environmental Protection Agency (EPA), and public drinking water branches have done a fair amount of research and screening to quantify each category of emerging contaminants, including disinfection byproducts (DBPs), pharmaceuticals and personal care products (PPCPs), pesticides and herbicides, cyanotoxins, endocrine disrupting chemicals (EDCs), persistent organic pollutants (POPs), micro-constituents, and others. Several key reviews have covered progressive studies on emerging contaminants in source waters and drinking waters in the past years [1-9]. Several organizations, such as EPA, American Water Works Association (AWWA), and Potomac Water Source Protection Partnership (Potomac DWSPP’s), and many others, have taken proactive actions in providing funding to support and promote research on emerging contaminants in natural water resources and drinking waters, and organizing workshops and meetings to deliver messages to the public. In addition, the findings and occurrence data of significant emerging contaminants, often called “contaminants of emerging concern” (CECs), are reported in the annual reports for public review.

To minimize levels of these emerging contaminants, the US EPA has finalized its Contaminant Candidate List 3 (CCL3) in 2009, which is composed of a total of 116 drinking water contaminants. These 116 contaminants have already been detected in public water systems in the US and/or pose the risk of existing in public water supplies. Under the Safe Drinking Water Act (SDWA), the EPA is required to evaluate and determine whether to regulate at least five contaminants from the CCL every five years. Also, the EPA is required to issue a new list of no more than 30 unregulated contaminants to be monitored by public water systems (PWSS) every five years. The data in Unregulated Contaminant Monitoring Rule (UCMR) has been used in regulatory determinations as well. Currently, UCMR3 has been published and UCMR2 compounds may be regulated in the near future. The critical issue is that once those emerging contaminants are regulated, all of the drinking water systems will be required to monitor those contaminants regularly.

In this review, the recent publications related to analytical method development, assessment, and removal of emerging contaminants in natural water resources and drinking water will be summarized to provide relatively comprehensive information to the researchers in this field. However, due to the large variety of lists of emerging contaminants, it is not possible for this review to cover all of them. This review mainly focuses on the following four groups of chemical contaminants: pharmaceuticals and personal care products (PPCPs); major disinfection byproducts, cyanotoxins, and pesticides and herbicides. The publications pertinent to specific water treatment technologies (such as free chlorine, monochloroamine, permanganate, ozone, UV, etc.), health risk assessments and ecological impact are not included in this review. In addition, literatures pertinent to emerging contaminants in air and other environments are also not covered in this review.

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Assessment and Removal of Pharmaceutical and Personal Care Products (PPCPs) in Source Water and Drinking Water

Pharmaceuticals and personal care products (PPCPs) are used for a wide variety of applications for human and veterinary uses. Human pharmaceuticals of great interest include; analgesics, antibiotics and antimicrobials, anticonvulsant/antiepileptics, antidiabetics, antihistamines, antipsychotics, antidepressants, antiangiety drugs, beta-blockers (β-blockers), cytostatics and antineoplastics, estrogens and hormonal compounds, lipid-regulators, stimulants, and X-ray contrast media. These compounds may be excreted directly or partially metabolized, resulting in their eventual passage into the environment. There are many routes to transport PPCPs into our natural water resources, such as improper disposal from individuals, residues from hospitals and veterinary drug use for animal farms (cattle, pigs, turkey, chicken, and others), residues from pharmaceutical factories (well defined and controlled), and so on. In the past decades, the issues of PPCPs in natural waters pertaining to the human usage, especially for antibiotics and steroids, were largely over looked. U.S. Geological Survey published a study in 2002 brought attention to PPCPs in water. Detectable of PPCPs were found in around 110 out of 139 susceptible streams in 30 states [10].

A recently published occurrence study [11] revealed that some PPCPs were detected in untreated and treated water samples collected across Missouri, of which caffeine was detected at concentration of 224 ng/L. Even though the potential adverse effects on human by drinking water have attracted more and more attention, there is no specific water treatment plants equipped with PPCPs removal technology. It was reported that the average concentration of aspirin is 0.22 μg/L in some water treatment facilities in Germany, and the aspirin concentration can reach up to 13 μg/L in some water treatment facilities in Greek and Spain [12-16]. Benotti et al. [17] have screened a diverse group of pharmaceuticals, potential endocrine disrupting compounds (EDCs), and other unregulated organic contaminants from 19 U.S. water utilities for 51 compounds, and 17 pharmaceuticals and 12 EDCs (Table 1). Due to the large variety of PPCPs that may have been transported to our natural water resources, the assessment and removal of PPCPs in source water or drinking water becomes important as there is uncertainty about their risk to the environment and human health.

Conventional detection methods, such as UV/Vis is absorption detection and fluorescence detection, cannot meet the needs for detecting μg/L or ng/L levels of PPCPs in water samples. Mass spectrometry (MS) hyphenated with other separation techniques have been widely used for PPCPs assessment in water samples. For example, determination of trace levels of PPCPs and EDCs has been accomplished by using gas chromatography-mass spectrometry (GC-MS) with derivatization [18]. The major limitations of GC are that samples must

<table>
<thead>
<tr>
<th>Compounds</th>
<th>Source</th>
<th>Finished</th>
<th>Distribution</th>
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<tbody>
<tr>
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<tr>
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<td>&lt;MRL</td>
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<tr>
<td>Testosterone</td>
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</tr>
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Table 1: Method reporting limits (MRLs), maximum concentration (max), median concentration (med) of pharmaceuticals and EDCs in source water, finished water, and distribution systems. All concentrations are presented in ng/L. (The data were from Benotti et al. [17]).
be volatile and thermally stable, which restrict this analytical technique to only certain PPCP compounds. Instead, liquid chromatography-mass spectrometry (LC-MS) and liquid chromatography-tandem mass spectrometry (LC-MS/MS) have become popular analytical techniques for PPCPs analysis. A variety of LC-MS or LC-MS/MS methods have been developed and applied for simultaneous analysis of several or many PPCP compounds in different types of water due to their high sensitivity, high accuracy, and high throughput [11,19-25]. Previously, UV-filtering compounds that are used in sunscreens, cosmetics, and other personal care products had mostly been measured using HPLC/UV. In 2008, a new LC-MS/MS method for analysis of nine UV filter compounds in seawater, river water, and wastewater was developed with detection limits of 7-46 ng/L [26].

Recently, Wang et al. have developed a new HPLC-MS/MS method that can simultaneously quantify 16 pharmaceutical compounds in a single run with the method detection limits (MDLs) of 0.3-4.3 ng/L [11,24]. The method has been used to analyze PPCPs in different types of water samples, including: Mississippi River, Missouri River, lakes, reservoirs and deep wells, and 11 pharmaceuticals were identified, mostly in surface water samples. Due to the very low PPCP concentrations in water, pre-concentration using solid phase extraction (SPE) is often necessary to enrich the target PPCP compounds before HPLC-MS/MS analysis. Up to date nearly all SPE was performed by following US EPA method 1694 [27], but with different modifications according to the specific application. Even though, low recoveries for some of the PPCPs are unavoidable when large numbers of PPCPs are analyzed in a single sample because of the different retention efficiencies of PPCP compounds onto the cartridge. Therefore, isotope-labeled internal standards are often applied to the water sample preparation to account for the low recovery of some compounds and to enhance data accuracy [11,27].

Removal of PPCPs has become a key concern in emerging contaminant control and drinking water protection. Until now, there is no comprehensive method to eliminate different categories of PPCPs from waters. The elimination of a specific analyte or a group of similar chemicals has been reported [16,24,28-37]. However, the removal efficiency may vary significantly among different PPCP compounds. For example, chlorination treatment can degrade sulfamethoxazole almost completely but it is not effective for carbamazepine [34]. Most water treatment plants utilize oxidation systems, such as free chlorine, ozone, and permanganate, monochloramine, or UV radiation during the water disinfection process. In addition, periodic powdered activated carbon (PAC) adsorption and two-stage lime softening are often used as part of the treatment process. Studies showed that both oxidation and PAC can remove some of the PPCP compounds [24,35-38]. Carballa et al. reported the removal of more than 80% sulfamethoxazole and natural estrogens, and more than 60% removal of galaxolide using ozone as the oxidant [39]. While efficient removal (~99%) was achieved by granular activated carbon (GAC), researchers have also investigated the removal efficiency of PPCPs in water by using reverse osmosis (RO) membrane filtration and nanofiltration (NF) with over 95% of removal [40]. Recently, Wang et al. [24] investigated the removal efficiencies of eight pharmaceuticals (caffeine, acetaminophen, carbamazepine, sulfamethoxazole, trimethoprim, erythromycin, lincomycin, and codeine) as a function of treatment approaches, types of disinfections (free chlorine, ozone, monochloramine, and permanganate). Their results showed that the oxidative removal of these pharmaceutical compounds varied significantly with different oxidation processes. Overall, chlorination was highly effective in the elimination of most of these pharmaceuticals and sample matrix, and pH caused notable differences in oxidation efficiency. Permanganate was also effective to decompose some pharmaceuticals. Ozone was a fast oxidizer but was very unstable. The ozone-removal was completed in about 2 minutes under the selected conditions. Chloramination was mostly ineffective in removal of all studied pharmaceuticals at typical dosage (3 mg/L) [24]. Parallel studies on different water matrices indicate that the oxidations preceded similarly but with a relatively slower rate in the surface water due to matrices effects. So far this work has shown that some oxidation systems may be useful in eliminating some of the PPCPs in water treatment facilities. The data on PPCP removal using Norit HDB PAC at normal dosage (2 mg/L) showed that most pharmaceuticals were not removed from the river water even when the equilibrium was reached after 24 hours. This comparison indicates that the sample matrix played an important role in the removal of pharmaceuticals from surface waters.

In conclusion, coagulation and filtration in conventional drinking water treatment processes are not adequate to remove PPCPs from the source water. The disinfectants used in water treatment, such as free chlorine, monochloramine, permanganate, ozone, UV, can only remove some of the PPCPs. Up to date; no single treatment process will completely remove all PPCPs from source water to non-detectable concentrations. Removal of PPCPs from natural waters and drinking waters is very challenging and more research needs to be done and new technologies need to be discovered or invented.

Assessment and Removal of Emerging Disinfection Byproducts in Drinking Water

In order to remove pathogenic microorganisms, water disinfection has been applied to the drinking water system since the early 1900s, and has become one of the most important treatments for drinking water [42]. However, the disinfectants commonly used may react with natural organic matter (NOM) and other chemicals (either natural or man-made products) present in the water to produce disinfection by-products (DBPs), which may be a threat to human health. More than 600 DBPs have been identified so far [2]. Trihalomethanes (THMs), haloacetic acids (HAAs), bromate and chlorite are already regulated by the EPA. Perchlorate has been decided for regulation by EPA, but its limit level has not yet been agreed. Several groups of emerging DBPs have been reported, including halonitromethanes, N-nitrosamines, haloacetanilides, halomales, halofuranones, among others.

Biannual periodic reviews on emerging drinking water contaminants, including emerging DBPs, have been published by Richardson [2-8]. In this review, only the most recent publications will be included. One of the most actively studied DBPs is the N-nitrosamine group because of the high toxicity of these compounds. The most frequently detected N-nitrosamine in drinking water is N-nitrosodimethylamine (NDMA). It was discovered initially in chlorinated drinking waters from Ontario, Canada [43]. According to surveys conducted across Asia and the Americas, NDMA is present at...
the low ng/L level in both source water (surface and ground water) and drinking water [44-46]. A specific review on nitrosamines summarized the formation of NDMA and related analogues [47]. Chloramination with a high concentration of N-nitrosamine precursors present in water could result in elevated NDMA formation. Recently, Wang and Cheng et al. [48,49] developed a fast and sensitive HPLC-MS/MS method for simultaneous quantitative analysis of nine N-nitrosamines and four precursors in drinking water. Their MDLs in water ranged from 0.05 µg/L to 5 µg/L without any preconcentration procedures. Wang and Ren et al. [46] developed a method to analyze nine nitrosamines with a MDL ranging from 0.2-0.9 ng/L for the source water samples and 0.1-0.7 ng/L for the finished water samples.

Since DBPs are generally present as a complex mixture in the drinking water treatment system at concentrations from low ng/L (ppt) to µg/L (ppb) levels, it makes separation and detection of DBPs more challenging. Several reviews on the detection of DBPs in drinking water have been published [50-52]. For the DBPs with low molecular mass, thermally stable, and volatile or semi-volatile characteristics, GC methods have played an essential role in the analytical measurements of these compounds. Electron capture detector (ECD) is one of the most commonly used detectors in GC for analysis of compounds with electron-withdrawing groups. Pre-concentrate preparation methods such as SPE, liquid-liquid extraction, and solid phase micro extraction (SPME) are generally used to concentrate the analytes. Because of the large GC-MS database library existing for many organic compounds, which make identification of unknown compounds much easier, GC-MS has also become a key technique for DBP discovery and quantification. Over the last 25 years, hundreds of DBPs have been identified, mostly through the use of GC-MS. However, the use of GC-MS is limited or of no use when the target DBPs have high molecular mass, such as over 1000 Da after derivatization, are non-volatile or very polar (e.g. ionic DBPs). One way to overcome this limitation is by derivatizing the analytes to make them volatile, but this can be difficult for some compounds. Therefore, the applications of HPLC-MS or HPLC-MS/MS provide a better way to analyze DBPs with high molecular weight and/or high polarity in water samples without derivatization.

Ion chromatography-inductively coupled plasma-mass spectrometry (IC-ICP-MS) is also suitable for the analysis of some DBPs such as iodoacetic acids, bromoacetic acids, and bromate. Recently, Shi et al. have developed a new rapid and sensitive method for simultaneous analysis of six brominated and four iodinated acetic acids, bromate, iodate, bromide, and iodide using IC-ICP-MS [53]. The method detection limits (MDLs) in natural water ranged from 0.33 to 0.72 µg/L for iodine species, and from 1.36 to 3.28 µg/L for bromine species.

Because of the arising concern for human health risks of DBPs in drinking water, control and removal of DBPs are necessary. One commonly used approach is to prevent the formation of DBPs in the first place by removal of the DBP precursors, in which coagulation and ion exchange could be used [54]. Adsorption by GAC and PAC has also been used to remove some of the DBPs and their precursors from the water. Recently, Cheng et al. [49] have examined three different types of PACs, namely bituminous coal-based WPH, lignite coal-based Hydro Darco B (HDB), and wood-based Aqua Nuchar (AN), for their adsorption capacity for the studied N-nitrosamines at all pH levels, even with dosages of up to 10 mg/L in both DI and natural water. Although nitrosamines formation during water treatment sometimes occurred in the distribution systems, these results still have significant implications whenever there are high nitrosamine levels in the water treatment plant influents, especially those that are fed from upstream wastewater discharges. In addition, removal of nitrosamines by nanomaterials has been explored. Wang et al. [48] have tested three different types of activated carbon nano-particles (NPs) from bamboo, charcoal, and coconut shell as raw materials. The removal experiments were carried out at two different pH (6.6 and 8.6). Coconut shell-based activated carbon NPs had better removal efficiency for this group of compounds than the other two activated carbon NPs. The removal efficiency in reagent water was as high as 50%, with a typical dosage of 2 ppm activated carbon NPs, at a typical contact time of 4 hours. In pre-filtered river water, the removal efficiency was a little lower due to competition from NOM. No significant differences between the two selected pH values were observed.

Advanced oxidation processes (AOPs) have also been suggested as appropriate techniques to remove the NOM from drinking water [55]. Other techniques, such as membrane filtration and ion exchange are also applicable options [56]. Carbonized electro spun nano fibrous membranes have shown effective removal of some DBP’s removal from drinking water. It has also been reported that anion exchange can effectively remove DOM from solution and reduce DBP formation during chlorination [57]. While effort has been made to control and remove currently known DBPs, we are still facing great challenges on numerous unknown DBPs. Thus, more research need to be conducted and sensitive analytical methods need to be developed to monitor and effectively remove DBPs from drinking water.

Assessment and Removal of Cyanotoxins in Source Water and Drinking Water

Known as blue-green algae, Cyanobacteria are photosynthetic microorganisms found in lakes, streams and ponds. There are thousands of cyanobacteria species about half of which produce toxins. A variety of cyanobacteria and their toxins have been identified and their occurrence has been reported in fresh, brackish and marine waters all over the world. The presence of cyanotoxins in surface or drinking water may cause serious health risks to humans and animals. For example, hepatotoxins affect the liver and kidney, neurotoxins affect the central nervous system, and dermatotoxins, which are skin irritants, are capable of causing both acute and chronic illnesses. Based on toxicological, epidemiology and occurrence studies, the EPA Office of Ground Water and Drinking Water has restricted its efforts to 3 of the over 80 variants of cyanotoxins reported, recommending that microcystins congeners LR, YR, RR and LA, and cylindrospermopsin be placed on the Unregulated Contaminant Monitoring Rule (UCMR) [58-70]. Table 2 summarizes the effectiveness of various types of treatment for removal of intact cyanobacteria cells and treatment processes that are effective in removing extracellular dissolved toxins of several of the most important cyanobacteria.

Among the major cyanotoxins, saxitoxins are a large family, better known as the paralytic shellfish poisoning toxins. These toxins have comparable toxicity to some toxicogenic marine dinoflagellates that accumulate in shellfish feeding on those algae. Saxitoxins have been reported in freshwater cyanobacteria such as Aphanizomenon spp. and...
Study data is scarce; it is assumed that membranes would be effective for removal of intracellular cyanotoxins. Microfiltration is not effective with doses used in drinking water treatment. Effective for the removal of intracellular toxins when cells accumulated in sludge are isolated from the plant and the sludge is returned to supply after sludge separation. Membranes study is scarce; it is assumed that membranes would be effective for removal of intracellular cyanotoxins. Microfiltration and ultrafiltration are effective when cells are not allowed to accumulate on membranes for long periods of time. Flotation processes, such as Dissolved Air Flotation (DAF), are effective for removal of intracellular cyanotoxins since many of the toxin-forming cyanobacterial cells are buoyant. Avoid because often lyses cyanobacterial cells releasing the cyanotoxin to the water column. Effective for oxidizing microcystins and anatoxins. Further research is needed for cylindrospermopsin. Flotation processes, such as Dissolved Air Flotation (DAF), are effective for removal of intracellular cyanotoxins since many of the toxin-forming cyanobacterial cells are buoyant. Effective for oxidation extracellular cyanotoxins as long as the pH is below 8, ineffective for anatoxin-a. Flotation processes, such as Dissolved Air Flotation (DAF), are effective for removal of intracellular cyanotoxins since many of the toxin-forming cyanobacterial cells are buoyant. Avoid because often lyses cyanobacterial cells releasing the cyanotoxin to the water column. Membranes depend on the material, membrane pore size distribution, and water quality. Nanofiltration and ultrafiltration are likely effective in removing extracellular microcystin. Reverse osmosis filtration would likely only be applicable for removal of some extracellular cyanotoxins like cylindrospermopsin. Cell lysis is highly likely. Further research is needed to characterize performance. Effective for oxidizing microcystins and anatoxins. Further research is needed for cylindrospermopsin. Very effective for oxidizing extracellular microcystins, anatoxin-a and cylindrospermopsin. Not effective with doses used in drinking water treatment. Effective for oxidation extracellular cyanotoxins as long as the pH is below 8, ineffective for anatoxin-a. Effective for degrading microcystins and cylindrospermopsin but at impractically high doses. PAC: Most types are generally effective for removal of microcystin, anatoxin-a and cylindrospermopsin, especially wood-based activated carbon. GAC: Effective for microcystins but less effective for anatoxin-a and cylindrospermopsins.

**Table 2: Summary of treatment process and effectiveness for removal of intact cyanobacteria cells and extracellular dissolved toxins.** Adapted with permission from EPA report [71].

*Lyngbya wollei* [71,72]. Cylindrospermopin was firstly identified in the species *Cylindrospermopsis raciborskii* which have begun to rapidly increase and dominate some Florida water bodies since 1997. This cytotoxic alkaloid is highly water soluble and stable to relative extremes of temperature and pH [72-77]. Microcystins are the most abundant cyanotoxins which can be produced by various cyanobacteria such as *Microcystis, Anabaena* and *Nostoc*. Microcystins have been surveyed in many countries including Australia, Canada, China, Holland, and US, and the toxin levels were reported from 0.3 to 80 µg/L, of which MC-LR is the most common and toxic, making up 45.5% to 99.8% of total micro cyanists found in natural waters [59,67,73].

Continually advancing technology fulfills the immediate need for both screening and confirmatory methods for the cyanotoxins analyses. Traditionally, different analytical methods such as UV detection (for toxins with UV chromophore), fluorescence detection for saxitoxins [78], GC-MS for anatoxin, static Fast Atom Bombardment mass spectrometry [79] and on-line Continuous flow-Fast Atom Bombardment mass spectrometry detection for microcystins [80,81], were required for studying different classes of cyanobacterial toxin. Mass spectrometry, unlike UV spectroscopy, has the advantage that it can handle compounds lacking the UV chromophore. Furthermore GC-MS is applicable to study anatoxin-a, although samples have to be derivatized before analysis [82]. The most sensitive technique currently used for the analysis of trace-level concentrations in water samples involves liquid chromatography-mass spectrometry, specifically liquid chromatography - tandem mass spectrometry (LC-MS/MS), which has been widely applied in environmental analysis [83,84]. A range of LC-MS/MS methods for cyanotoxins have been developed [85-88], and most of these methods are dependent on sample cleanup methods. Bogiali et al. firstly reported a SPE-LC-MS/MS method for measuring microcystins and cylindrospermopin with limits of quantification within 2-9 nL/L range [87], and one year later Hiller et al. developed a method in precursor ion mode by LC-MS/MS to detect the maximum number of cyanobacterial toxins from different toxin groups in a single chromatographic separation, and a detection limit of 9 pg for cylindrospermopin could be achieved [88]. Very recently, Cheng et al. developed a fast and easy method for quantitative analysis of nine major cyanotoxins using LC/MS/MS without sample cleanup processes [89].

Due to increasing occurrence and high toxicity, effective treatments strategies are needed to prevent cyanotoxins inform reaching the drinking water. Conventional treatments commonly used include both chemical and physical procedures, such as various oxidants, UV irradiation or coagulation. Experimental and full-scale studies for removal of cyanobacteria using membranes are scarce. In general, micro- and ultra-filtration membranes could be expected to remove cyanobacterial cells effectively [90-92]. The treatments mentioned above will not remove extracellular or dissolved toxin to a significant extent. Most of the microcystins are well removed by activated carbon [93,94], the exception being MC-LA, but for other Microcystins wood-based chemically activated carbon is the most effective treatment. GAC filtration displays a limited lifetime for all toxins, due to eventual saturation of the filters. In addition to filtration, dissolving microcystins have been removed by some reverse osmosis and nanofiltration membranes [95,96]. Chlorination and ozonation are also effective for removal of microcystins. A residual of at least 0.3 mg/L of ozone for 5 minutes will be sufficient for removing all the most common microcystins [92,97-100]. Cheng et al. examined several oxidative and UV irradiation disinfection treatments for removal cylindrospermopin and its source micro-organisms, *Cylindrospermopsis raciborskii* [82]. Ozone and free chlorine were highly effective at the removal both of cylindrospermopin and of *Cylindrospermopsis raciborskii*. Chlorinated dioxide, monochloramine, permanganate, and UV irradiation at typical water treatment dosages were all ineffective at removing cylindrospermopin. Chlorinedioxide, monochloramine, monochloramine, and permanganate were each only capable of partial inactivation of *Cylindrospermopsis raciborskii*. This information provides a basis for removal of both *Cylindrospermopsis raciborskii*.
and cylindrospermopsin in water treatment plants. An interesting argument was discussed in a recently published work by Shi et al. on the impacts of pH as well as NOM concentrations on the adsorptive efficiency of PAC for saxitoxin treatment, which reinforce the critical role of PAC sorption performance on water quality [101].

Assessment and Removal of Pesticides and Their Degradation Products in Source and Drinking Water

The widespread use of insecticides, fungicides and herbicides over the past 60 years has led to increased occurrence of pesticide residues in all types of water resources, including drinking water and water for recreational purposes. Degradation of these pesticide residues may occur in environmental waters by natural processes of hydrolysis, photolysis and biological remediation carried out in situ [102]. In addition to these natural processes, remediation through different treatments includes chemical oxidation, photolysis with UV, hydrolysis at acidic or alkaline pH, biodegradation by microbes and phytoremediation [103-110]. The degradates of these pesticides in a wide variety of water supplies have also been detected. Toxicity of degradates can in some cases be equal or greater than that of the parent compounds [111-113]. Thus, the investigation of pesticide degradation by-products is an emerging research area in the field of water quality.

A number of analytical methods have been developed for detecting the large variety of pesticides residues found in waters. HPLC-MS, HPLC-MS/MS, GC-MS, and GC-MS/MS have been commonly used for analysis of pesticides and their degradation by-products [114-123], either with direct sample injection, or after SPE or liquid-liquid extraction (LLE) [114]. LC-MS/MS is currently becoming the most powerful technique because of its excellent sensitivity, rapid analysis, and little sample preparation compared with previous GC and HPLC analytical techniques. Recent developments of ultra-pressure liquid chromatography (UPLC) and enhanced ion-trap function of MS will further advance the UPLC-MS/MS technology for its applications in water research and many other fields. The recent availability of LC columns with smaller particle size also contributes to higher resolution and speed of analysis for both LC/MS and UPLC techniques. A number of quantification and identification methods using LC-MS/MS have been developed and applied to analysis of pesticides and their degradation products in drinking water and source water [84,115-117,121-125]. The methods have been used for occurrence studies, degradant identifications, reaction pathway elucidation, and kinetic investigation. It is anticipated that LC-MS/MS technique will continue to play a most important role in drinking water and source water research in the near future.

Screening studies of widely used pesticide and their degradants in drinking water and source water have been conducted under general water treatment conditions. One such comprehensive study focused on the reactivity of a set of 62 pesticides from 14 different classes: acid compounds, amides, carbamate insecticides, dinitroanilines, isoxazoles, organochlorins, organophosphorus insecticides, phthalate, pyrazole, triazines, urea herbicides, thiazole, triazine, and pyrethroids [115,117,125]. The general disinfection treatment methods in this study included oxidation by six oxidants (free chlorine, monochloramine, chlorine dioxide, hydrogen peroxide, and UV), photodegradation by UV, and hydrolysis under different pH (2, 7, and 12). Pesticides and their degradates were analyzed by LC-MS, LC-MS/MS, and GC-ECD, with methods having MDLs at ng/L levels. The MDLs by LC-MS via direct injection of samples were in the range of 16 ng/L to 493 ng/L, and MDLs by GC-ECD were 12 ng/L to 139 ng/L after LLE. Many pesticides were found to be reactive via hydrolysis and/or chlorination and ozonation under typical drinking water treatment conditions, less reactive with chlorine dioxide, monochloramine, hydrogen peroxide, and UV. Forty percent of the pesticides were highly reactive with one or more oxidants, while 60% were at least moderately reactive. Organophosphorus and carbamate insecticides/herbicides were the most reactive classes overall, while others were found less reactive.

Sulfonic acid (SA) and oxanilic acid (OA) degradates of herbicides were shown to be more persistent and mobile than their parent compounds [126-129]. A screening study of herbicide degradation by-products of metolachlor, alachlor, acetochlor, and propachlor in a variety of water treatment plants has been performed by using a very rapid and sensitive LC-MS/MS method developed by Cheng et al. [117]. Eight ESA and OA major degradation products were analyzed at detection limits of 40-50 ng/L, the lowest detection limited reported without sample pre-concentration. Screening of these degradation products from both source water and treated water of 34 water treatment facilities in Missouri was conducted for both winter and summer seasons. The water resources include river water, lake water, reservoir water, and underground water. All the herbicide degradants were not detectable in the water collected in winter season while some degradants were detected in the water collected during summer season, at concentration range from none detectable to 60 ng/L. Missouri River and Mississippi River water resources were found to have more herbicide degradants than the other water resources tested. Another comprehensive full-scale study was conducted for atrazine, simazine, and propazine [130]. About 900 paired source water and treated drinking water samples were analyzed by GC-MS method for the parents and the degradants of these herbicides. Atrazine concentrations were generally below the established 3 µg/L, maximum contaminant level (MCL) and that simazine and propazine concentrations were generally non-detectable. Degrant chloro-s-triazine was detected in both source water and already treated water. PAC is effective (~95% removal) for the removal of atrazine and the degradant [131].

The organophosphorus insecticide dyfonate (active ingredient fonofos) is most widely used to control Lepidoptera and all other insect pests. Like most organophosphorus compounds, high hydrolysis rate was observed during screening studies [116,118,126]. A comprehensive investigation on the hydrolysis of dyfonate and its degradation products in alkaline aqueous solution was conducted by Wang et al. [122]. The hydrolysis product of dyfonate at elevated pH (10, 11, and 12) was investigated in phosphate buffered water over the course of 7 days. Two major hydrolysis degradation products, thiphenol and phenyl disulfide, were separated, identified, and quantified using LC/MS/MS, HPLC-PDA and GC-MS methods. Dyfonate hydrolysis products were reported highly pH dependent. The transformation pathways and pH effect were suggested as the following illustration (Figure 1).

The disinfection byproducts of dyfonate via various oxidation treatments including free chlorine (FC), hydrogen peroxide (H₂O₂), monochloroamine (MCA), chlorine dioxide (ClO₂), ozone, and permanganate were also investigated by the same group of researchers [122]. Dyfonate oxygen analog (phosphonothioic acid) was identified as the primary oxidation byproduct by FC, ozone, MCA, and H₂O₂ treatment in the following pathway, while no oxidation byproduct was detected in the ClO₂ and permanganate oxidation system. It was suggested that this degradant is more difficult to remove from water than the parent compound dyfonate. However, the degradant was less toxic.
Proposed degradation pathways of aldicarb by various oxidants. Based on this systematic study, if aldicarb was indeed transported further to N-chloro-aldicarb sulfone by FC. Degradation pathways of aldicarb by different oxidants were proposed as shown in Figure 2. All oxidants have been determined and the reaction rates are higher under higher pH from all the oxidation treatments. Half-life and reaction rate constants of the degradation of fipronil at pH 6.6 and 8.6 for tested oxidants have showed that only FC and ozone can oxidize molinate, while other oxidants and UV did not show significant removal of this herbicide. Diazinon can be rapidly converted to the active diazoxon and the degradate IPMP during FC and ozone disinfection (Figure 3). Both compounds are stable to further FC oxidation at typical water disinfection conditions, but the oxon form is more toxic than the parent compound. In fact, it is the active insecticidal compound, which inhibits acetylcholinesterase in all animals [142]. On the other hand, both compounds are labile to further oxidation by O₃ and, hence, they may be further converted to unknown degradates during ozonation.

Dimethenamid, a chloroacetamide herbicide used to control grasses was also studied in detail under drinking water treatment conditions [126]. Among the disinfection treatments by FC, MCA, ClO₂, H₂O₂, and UV₂₅⁴, Dimethenamid can only be degraded by FC and O₃, while the other oxidants did not show significant removal of dimethenamid. Chloro-dimethenamid was identified as the major product of FC treatment, while different degradant was found by ozonation (Figure 4). All of the other oxidants had low levels of dimethenamid removal and no degradation products were detected.

which are the two majorly used oxidation systems in drinking water treatment plants.

Molinate is a thiocarbamate herbicide widely used in agriculture. Occurrence studies indicated that molinate contamination exists in many natural water systems including river waters [137], rain water, ground water, and surface waters [138-141]. The removal efficiency of molinate by various oxidants and identification of the degradates of molinate in drinking water system have been systematically investigated using LC-MS/MS [121]. The oxidants tested were FC, MCA, ClO₂, permanganate, H₂O₂, ozone; and UV radiation. Research has showed that only FC and ozone can oxidize molinate, while other oxidants and UV did not show significant removal of this herbicide. A kinetic study showed that the degradation of molinate with free chlorine treatment was extremely fast [121]. Hexahydro-1-H-azepane-1-carboxylic acid was identified as the major degradate of molinate after treatment with free chlorine and ozone. This degradant is more resistant to free chlorine in the same treatment. A possible degradation reaction of molinate was suggested in that study.

Fipronil is a phenylpyrazole insecticide, increasingly being used in place of organophosphates, pyrethroids, carabmates, and many cyclodienees. However, fipronil is more persistent in soil and water than the former compounds [132], and this poses a problem for water quality. The oxidation and degradation of fipronil during drinking water treatment has been investigated under various water oxidation conditions including FC, MCA, ClO₂, and MnO₄⁻, and the kinetic rate of fipronil and fipronilsulfone were determined [117]. Fipronil was degraded quickly by treatment with FC, ClO₂, and MnO₄⁻. However, the common reported degradates (including fipronilsulfone, fipronil sulfide, and fipronildesulfinyl, all of which are as toxic as the parent compound) were not detected after treatment with FC and ClO₂, by using the LC-MS analytical method. One degradant fipronilsulfone was identified from the treatment of MnO₄⁻. Oxidation of fipronil by MCA was very slow or insignificant in the tested period of seventy minutes. The half-life of the fipronil degradation by MCA was 3.1x10⁴ min at pH 6.6 and 3.1x10³ min at pH 8.6, respectively. Half-life and reaction rate constants of the degradation of fipronil at pH 6.6 and 8.6 for tested oxidants have been determined and the reaction rates are higher under higher pH from all the oxidation treatments.

Aldicarb is a carbamate class pesticide. As a result of widespread usage, aldicarb and its metabolites have been detected in drinking water systems in several countries, and cases of human poisoning have occurred [133]. Ozone and free chlorine treatments were investigated for degradation of aldicarb in 1990s [110,134]. Recently, a systematic study of aldicarb and its metabolites was conducted involving treatment with various oxidants in water, with analysis by HPLC-MS and HPLC-UV [124]. Free chlorine, high-dosage UV radiation and permanganate were very reactive with aldicarb, whereas chlorine dioxide showed weak oxidation. Aldicarb sulfoxide was identified as a major degradation product of aldicarb by oxidation with FC, MCA, ozone, and hydrogen peroxide, while aldicarb sulfone was identified as an oxidation byproduct of both aldicarb and aldicarb sulfoxide by permanganate treatment. Aldicarb sulfone was found to degrade further to N-chloro-aldicarb sulfone by FC. Degradation pathways of aldicarb by different oxidants were proposed as shown in Figure 2. All degradates are even more toxic than the parent insecticide [135,136]. Based on this systematic study, if aldicarb was indeed transported into the source water, aldicarb sulfoxide would be the major potential aldicarb degradates in drinking water after FC or MCA treatment,
Fungicides are widely used in agriculture to prevent the outbreak of persistent, significant plant diseases and also in several biocidal product types for material protection (treatment of wood, concrete, paints, and roofs) [143]. There are more than 67000 pesticide products currently registered for use in the United States, in which over 3600 are used for fungal diseases [144]. An estimate of 7-24% of the losses in yields to commodity crops such as potatoes worldwide was caused by fungal pathogens in 2001–2003 [145]. Serious concerns have been raised about the potential harmful effects of fungicides on aquatic ecosystems due to their persistence in soil and water [146] due to their stability towards hydrolytic, photolytic and biological degradation as well as their endocrine disrupting properties [147]. Pyrimethanil, an anilino-pyrimidine fungicide, has been classified as persistent organic pollutant [148] because of its high chemical and photochemical stability, and low biodegradability. Reilly et al. [147] has conducted occurrence study in three targeted use areas and some fungicides have been detected (Table 3).

Several sensitive analytical techniques have been developed to quantify fungicides in variety of environmental matrices, such as surface water, wastewater, sediment, sludge, and soil. A very concise review has covered some of the chromatographic determination of fungicides in biological and environmental matrices [149]. An ultra-high-performance liquid chromatography-tandem mass spectrometry (UHPLC-MS/MS) has been well developed to 19 biocides with quantification limits ranging from 0.01-8 ng/L and with a recovery range of 70-120% based on the matrices [150]. The method has been used to study the occurrence of these compounds in influent samples and 16 targeted compounds have been detected in the concentration range of 0.4-372 ng/L [150]. In addition, HPLC methods with UV detection have also been developed for determination of fungicides [151,152]. The methods have been used to determine benomyl, carbendazim, 2-aminobenzimidazole (2-AB), thiabendazole, and iprodione (I) in surface water. The detection limit ranges from 1-4 μg/L without preconcentration. By using on-line preconcentration, the detection limit for iprodione (I) can reach to 0.02 μg/L.

GC-MS methods for quantitative analysis of fungicide compounds are still powerful methods if the compounds are thermally stable and volatile. Reilly et al. [147] has developed a GC- ion trap mass spectrometry (GC/IT-MS) method for occurrence study of selected fungicides in surface and groundwater, and the method detection limits (MDLs) for all compounds in water ranged from 0.9 to 12.1 ng/L. Takagaki et al. [152] has developed a rapid and sensitive GC-MS method for analysis of dithiocarbamate fungicides (mancozeb, manebe, and polycarbamate) in environmental water samples with solid-phase micro-extraction. The linearity of the working curves was obtained in the concentration range from 0.3 μg/L to 10.0 μg/L for all compounds.

Several methods have been reported to remove fungicide. Papinutti et al. [153] have reported a novel way to remove triphenylmethane dye malachite green (MG), commonly used as fungicide, by using wheat bran (WB). The study results showed that the equilibrium was attained after 40 min of contact time (24 mg/g dry WB) and the maximum adsorption of dye occurred at pH range 7-9, where the amount of dye removed was nearly 90%. A phytoremediation technique of fungicides by aquatic macrophytes has also been reported [154]. The rate of removal of 2 fungicides (dimethomorph and pyrimethanil) from water by 5 macrophyte species (L. minor, S. polyrhiza, C. aquatica, C. palustris and E. canadensis) was assessed and the maximum removal rate during the 4-day test period was 48 μg/g fresh wt. (FW) for dimethomorph and 33 μg/g FW for pyrimethanil. Physical treatment to remove some fungicides have also been reported [155] by using primary (mech.), secondary (activated sludge), and tertiary (sand filtration and chlorination) treatments. The results showed that all the azole fungicides and pyrimethanil showed relatively low removal efficiencies after secondary and tertiary treatments. Average removal rates of the fungicides after secondary treatment ranged from 31% for pyrimethanil to 65% for triadimefon. The average overall removal efficiencies after tertiary treatment ranged from 46% for pyrimethanil to 93% for triadimefon.

Neonicotinoids are a group of insecticides that have been used extensively as commercial insecticide. Imidacloprid, the representative of the first generation neonicotinoid insecticides, was patented in 1985 by Bayer and was placed on the market in 1991. Imidacloprid is selective toxicity for insects over vertebrates [156] and it is the highest selling insecticide worldwide used to control insects on crops or for seed treatment as well as veterinary medicine against parasites in dogs and cats. Imidacloprid has high solubility in water (580 ppm), is hydrolytically stable, and has long aerobic soil half-life (520 days). Based on the previous studies, the common transformation product of Neonicotinoids, Imidacloprid [157–159] and acetamiprid [160] is...
6-chloronicotinic acid (6CNA). The presence of 6CNA was confirmed in soil [161]. Due to its widespread use, persistence, and aquatic toxicity, the potential for transport from agricultural fields to surface water is a concern [162]. Starner et al. [163] has conducted a screening of imidacloprid in three agricultural regions of California and the results showed that Imidacloprid was detected in 67 samples out of 75 surface water samples collected (89%). The concentrations exceeded the United States Environmental Protection Agency’s chronic invertebrate Aquatic Life Benchmark of 1.05 μg/L in 14 samples (19%). The data of occurrence of imidacloprid in surface water in other parts of the United States is still very limited or not available.

For assessment of neonicotinoids, a HPLC–MS/MS method has been developed for simultaneous determination of imidacloprid and the olefinic imidacloprid, guanidine, olefinic guanidine, urea metabolites in water samples [164,165]. The method detection limit (MDL) for imidacloprid was 0.010 μg/L; the reporting limit (RL) was 0.050 g/L. The blank-matrix spike recovery performances were 83%-114%. Several GC-MS methods were reported to determine imidacloprid and other neonicotinoids. Nguyen et al. [166] developed a GC-MS method for determination of imidacloprid and acetamiprid in soil samples. The MDLs were 0.005 and 0.007 μg/mL for imidacloprid and acetamiprid and the limit of quantification (LOQ) was 0.02 μg/mL. The method had a linear range of 0.05-5.0 μg/mL range and recoveries were 90.4-93.7% at 0.5-2 mg/kg spiking levels. A method for determination of imidacloprid in water and soil samples by GC-MS with selected ion monitoring was also reported by Vilchez et al. [167]. The method has an applicable concentration range of 5-20 μg/L. The MDL was 0.16 μg/L for water and 1 μg/kg for soil samples.

Some studies have been conducted to investigate the imidacloprid removal from environmental samples. Phytoremediation method was reported to remove imidacloprid from soil and water [168]. In this study, broadleaf plantain plant (Plantago major L.) was used in phytoremediation of imidacloprid. Viable whole broadleaf plantain plant in water solution reduced imidacloprid residues by 55.81-95.17%, during 1-10 days of exposure periods compared with 13.71-61.95% in water solution without the plantain. The results showed that the growing cells of short-rod gram-negative bacteria that isolated from the water solution containing broadleaf plantain plants was able to induce 93.34% loss of imidacloprid as a source of both carbon and nitrogen within a short period (48 hr) compared with 31.90% in an uninoculated medium. The half-life in soil planted with broadleaf plantain was much shorter than that of unplanted soil (4.8 days vs. 8.4 days). A separate study has demonstrated the degradation of imidacloprid in water by photo-Fenton and TiO2 photocatalysis [169]. The data showed that the degradation of 50 μg/L of imidacloprid can be achieved within 25 minutes by photo-Fenton and within 100 minutes by TiO2 photocatalysis.

The other removal methodologies for pesticides/herbicides and their degradation products include majorly activated carbon
Future Trends in Assessment and Removal of Emerging Water Contaminants

(1) Even though a tremendous amount of work has been accomplished in the development of analytical technologies and methods for assessment of variety of emerging contaminants in natural and drinking waters, a lot of work still needs to be done to conduct high throughput assessment of emerging contaminants efficiently and accurately at low levels. Removal of emerging contaminants in natural and drinking waters is even more challenging and have a long way to go before they can be quantitatively removed in feasible and economic ways. The following areas are recommended as the major focus for assessing and removing emerging contaminants in natural waters and drinking water. Development of new monitoring systems. New instrumental technologies and methods are still required for many emerging contaminants to allow researchers and water treatment facilities to conduct quantitative and high throughput screening of those compounds in trace levels economically. Once some of the emerging contaminants are regulated in drinking water, routine monitoring is required to make sure that the levels of the regulated compounds are under the established limits. However, most of the current technologies, such as UPLC-MS/MS coupled with SPE extraction, are not cost effective and most water treatment facilities, especially in developing countries, may not have the funds nor the expertise required to own such a technology for emerging contaminant screening. The water samples have to be sent to a central laboratory for screening at a huge cost.

(2) Research on new technologies for removal of emerging contaminants in waters will be another top priority in the future years. Once the regulated contaminants show up over the maximum regulated levels, action must be taken to reduce them to harmless levels. The first priority is to remove them from drinking water. However, no effective removal technologies have been discovered or invented to simultaneously remove all of the concerned contaminants up to date, even though some techniques have been demonstrated to remove certain contaminants to certain extent. Nanomaterials have great potential for emerging contaminant removal due to their large specific surface areas. However, they have to be immobilized onto macro-particles such as GAC or PAC to prevent releasing nanomaterials into drinking waters, or else it would create further problems. The removals of DBPs are even more difficult because extra steps must be taken to remove those compounds without adding unnecessary contaminants into the treated water. The best way may be finding efficient ways to remove the precursors of DBPs to prevent formation of DBPs during the disinfection process.

(3) Risk assessment of emerging contaminants. Some studies have shown that some of the emerging contaminants dealt with here are cytotoxic at low levels. However, risk assessments of some compounds are very difficult because of the low concentrations found in waters, and the lack of sufficient monitoring and toxicity data available at the moment. New risk assessment guidelines need to be developed and unified so that all researchers in this area are in the same spectrum, so that assessment data are comparable among different laboratories.

(4) Establish a comprehensive emerging contaminant database. It is well-known that the quality of drinking water and the number of contaminants depend heavily on the quality of the source water (except for disinfection byproducts). The quality of the source water in turn depends on water resources. For example, well water (i.e. ground water) may contain much less organic contaminants than surface water because surface water is more influenced by industrial activities, effluents of municipalities, runoff from agriculture, recreational activities, shipping routes, river bank structures, and so on. Therefore, establishment of a comprehensive emerging contaminant database for each geographic region will help utilize specific treatments to remove the targeted emerging contaminants.

(5) Finally, measurement, risk assessment, and removal of degradates of emerging contaminants will be another issue for researchers to deal with. During the disinfection process, some contaminants may be broken down and get transformed to different chemicals, which –as we have seen- might be even more harmful to humans and animals. Therefore, assessment and removal of the contaminant degradates is even more challenging because their concentrations are even lower than those of the parent compounds. Furthermore, the health risks to humans and animals may be different because of different chemical properties and modes of action. The techniques for removal of the contaminant degradates may also be totally different from their parent compounds because the solubility and polarity may vary significantly from their parental compounds. Much more efforts and time will be required to accomplish this task.

Concluding Remarks

Although emerging contaminant compounds occur in trace concentrations in waters, their adverse effects to aquatic organisms, animals, and humans cannot be underestimated due to their continuous release into the water systems. The assessment and removal of emerging contaminants and their transformation products in natural and drinking waters are challenging tasks because of the complexity of contaminants in water samples. However, tremendous progress has been made on assessment of many emerging contaminants due to the great efforts and times committed by many scientists working in different research fields. The future trends in assessment and removal of emerging water contaminants will be on the oxidation/degradation products and metabolites of emerging contaminants because they have not yet been fully documented. With the advanced analytical techniques we currently enjoy, these contaminants can be identified and quantified, providing more insight to the occurrence, formation, properties and pathways. Development of feasible techniques to removal these contaminants, including precursors, degradates, and DBPs, is also going to be one of the top priorities in the future years because feasible techniques need to be in place to remove them or at least reduced them below the regulated levels.
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