Review Article

Sensors Applied for the Detection of Pesticides and Heavy Metals in Freshwaters

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Water is essential for every life living on the planet. However, we are facing a more serious situation such as water pollution since the industrial revolution. Fortunately, many efforts have been done to alleviate/restore water quality in freshwaters. Numerous sensors have been developed to monitor the dynamic change of water quality for ecological, early warning, and protection reasons. In the present review, we briefly introduced the pollution status of two major pollutants, i.e., pesticides and heavy metals, in freshwaters worldwide. Then, we collected data on the sensors applied to detect the two categories of pollutants in freshwaters. Special focuses were given on the sensitivity of sensors indicated by the limit of detection (LOD), sensor types, and applied waterbodies. Our results showed that most of the sensors can be applied for stream and river water. The average LOD was 72.53 ± 12.69 ng/ml (n = 180) for all pesticides, which is significantly higher than that for heavy metals (65.36 ± 47.51 ng/ml, n = 117). However, the LODs of a considerable part of pesticides and heavy metal sensors were higher than the criterion maximum concentration for aquatic life or the maximum contaminant limit concentration for drinking water. For pesticide sensors, the average LODs did not differ among insecticides (63.83 ± 17.42 ng/ml, n = 87), herbicides (98.06 ± 23.39 ng/ml, n = 71), and fungicides (24.60 ± 14.41 ng/ml, n = 22). The LODs that differed among sensor types with biosensors had the highest sensitivity, while electrochemical optical and biooptical sensors showed the lowest sensitivity. The sensitivity of heavy metal sensors varied among heavy metals and sensor types. Most of the sensors were targeted on lead, cadmium, mercury, and copper using electrochemical methods. These results imply that future development of pesticides and heavy metal sensors should (1) enhance the sensitivity to meet the requirements for the protection of aquatic ecosystems and human health and (2) cover more diverse pesticides and heavy metals especially those toxic pollutants that are widely used and frequently been detected in freshwaters (e.g., glyphosate, fungicides, zinc, chromium, and arsenic).
1. Introduction

Seventy-one percent of our planet is covered by water which is a vital necessity to the organisms living on the earth. Even though freshwater only occupied less than 3% of all the water on earth, our daily life is more associated with freshwater than saltwater. However, many freshwater ecosystems have been polluted by anthropogenic activities including the three most dominating contributors: human settlements, industries, and agriculture [1–3]. For example, more than 100,000 chemicals (e.g., pesticides) are registered nowadays, and most of them are related to our daily life; these chemicals can inevitably enter freshwaters [4]. In addition, more than half of the total production of chemicals is harmful to the environment [5]. In Latin America, Africa, and Asia, 1/3, 1/7, and 1/10 of all the streams and rivers have already been affected by pathogen (e.g., fecal coliform bacteria), organic (e.g., biochemical oxygen demand (BOD)), and salinity (e.g., total dissolved solids (TDS)) pollution [6]. At a national scale survey, the water quality of ~1/3 of US' streams and rivers was assessed by the Environmental Protection Agency (EPA), and the results revealed that 55% of the streams were categorized as impaired. Bacteria, sediment, and nutrients were identified as the three most significant causes for stream pollution in this survey [7]. Freshwaters in developing countries such as China are facing more serious pollution situation. It was estimated that ~60% of China’s groundwater was classified as poor or very poor, and the number is even higher (~80%) in 17 northern provinces [8]. The impaired water quality negatively affected aquatic organisms and generates major threats to waterbodies, with great consequences on aquatic ecosystems at levels ranging from individuals to watershed [9–13]. More importantly, human health is also at risk if clean drinking water cannot be accessed [4]. It was estimated that the freshwater resources for 82% of the world’s population are under high levels of threats, and the situation is more serious in developing countries than in developed countries [14]. Consequently, more than 1/3 of the population in the world lacks safe drinking water [4]. Freshwaters (e.g., streams, rivers, lakes, and ponds) receive large quantity of various pollutants including pesticides [15], heavy metals [16], and nutrients [17]. It was estimated that 80% of municipal wastewater that flows into waterbodies is untreated, and millions of tonnes of heavy metals and other pollutants were dumped into waterbodies every year [18]. In China, human activities introduced 14.5 ± 3.1 mega tonnes of nitrogen to freshwaters each year which are 2.7 times of the predicted safety threshold [19]. Excess nutrients such as nitrogen and phosphorus in freshwaters usually lead to eutrophication, one of the most common reasons for water quality degradation [20, 21]. Many efforts have been done to improve the water quality of freshwaters via direct or indirect ways [22, 23]. Monitoring water quality in freshwaters is still the first priority for many ecological studies, water quality control, and restoration projects [24, 25].

Monitoring water quality is especially important for the provision of clean drinking water and the protection of aquatic ecosystems [26, 27]. After the development of decades, numerous kinds of sensors, including chemical sensors, biosensors, and electronical sensors, have been developed to detect water quality [28, 29]. A sensor is a device that is capable of providing selective quantitative or semiquantitative analytical information via a biological/chemical/electronical recognition element; it usually is composed of a transducer and a processor [30]. Generally, the requirements of water quality sensors are confined to many factors such as the waterbodies to be monitored, water quality parameters to be tested, and the objects of the monitoring system [31]. The projection of future sensors targets on higher sensitivity, rapid detection, smaller size, inexpensiveness, disposability, ease of manipulation, durability for longer time, and suitability for multiple environments. For example, in a newly published review, Parra et al. [29] summarized several requirements of physical sensors for precision aquaculture: low maintenance, low cost, low battery consumption, nonmetal, robust, water-proof, withstand biofouling, and no effects on aquatic organisms. Previous review papers focus on either one type/category of sensors [32] or one analyte (or one group of analytes) [33]. This review paper will focus on the sensors applied to test two of the most common pollutants in freshwaters, i.e., pesticides and heavy metals. The general contamination status of these parameters in freshwaters and a simple analysis of sensors are also discussed. The sensitivity of sensors (limit of detection (LOD)) and sensor types are especially discussed. The present review paper differs from previous review papers in the following ways: (1) we unified the unit of LOD to make the comparison between studies possible and visualized; (2) only the data collected from freshwaters were used; and (3) not only the sensor types but also the detected analyte categories were discussed.

2. Materials and Methods

2.1. Database Compilation. We build the database of pesticide sensors by searching Web of Science using the following topics: “sensor” and “pesticide or herbicide or fungicide or insecticide” and “freshwater or river or stream or lake or reservoir or pond”. Most of the collected papers were published during the last five years which composed almost half of the publications (2015-2019). The data collected before 2015 were mainly based on previous review papers [34–36]. For each publication, we extracted the following information: tested analytes, sensor types (e.g., biosensors and electronical sensors), LODs, and the applicable waterbodies. For the optical sensors, we included fluorescent sensors, luminescent sensors, and colorimetric sensors. The tested analytes were grouped into three categories of pesticides (i.e., herbicides, insecticides, and fungicides). All the units of LODs were unified as ng/ml. The same method was used to build the database of heavy metal sensors by replacing “pesticide OR herbicide OR fungicide OR insecticide” with “heavy metal”. For heavy metal sensors, we only collected data during the year 2017-2019 (updated until October) which composed ~1/3 of all the publications.
| Analytes | Sensor types | LOD (ng/ml) | Waterbodies | Ref. |
|----------|--------------|-------------|-------------|-----|
| Picloram | Bioelectrochemical | 5 | Paddy field water | [55] |
| Malathion | Biosensor | 1 | Tap water | [56] |
| Methamidophos | Biosensor | 0.01 | Tap water | [57] |
| Monocrotophos | Biosensor | 0.015 | River and tap water | [58] |
| Monocrotophos | Biosensor | 0.009 | Tap water | [57] |
| Methamidophos | Biosensor | 0.013 | River water | [57] |
| Monocrotophos | Biosensor | 0.012 | Tap water | [57] |
| Monocrotophos | Biosensor | 0.032 | River water | [57] |
| Bentazone | Electronical | 262.3 | River water | [59] |
| Carbaryl | Electrochemical | 5.3 | Wastewater | [60] |
| Heptenophos | Electrochemical | 2.8 | Lagoon water | [61] |
| Fenitrothion | Electronical | 2 | Tap water and farmland water | [61] |
| Carbofuran | Electronical | 2.8 | Lagoon water | [61] |
| Fenobucarb | Electronical | 2 | Tap water and farmland water | [61] |
| Paraaxon | Electronical | 2.8 | Lagoon water | [61] |
| Chlorpyrifos | Bioelectrochemical | 0.004 | Lake water | [63] |
| Chlorpyrifos oxon | Bioelectrochemical | 0.004 | Lake water | [63] |
| Atrazine | Electronical | 2.2 | River water | [64] |
| Atrazine | Electronical | 4.5 | River water | [65] |
| Atrazine | Electronical | 1.9 | River water | [66] |
| Atrazine | Electronical | 13 | River water | [67] |
| Atrazine | Electronical | 3.1 | River water | [68] |
| Atrazine | Electronical | 3.8 | River water | [68] |
| Atrazine | Electronical | 30.2 | Natural waters | [69] |
| Chlorpyrifos oxon | Bioelectrochemical | 1.1 | River water | [70] |
| Paraaxon | Bioelectrochemical | 30 | River water | [70] |
| Malaoxon | Bioelectrochemical | 25 | River water | [70] |
| Chloromequat | Bioelectrochemical | 502.74 | River and ground water | [71] |
| Carbofuran | Bioelectrochemical | 20 | Well water | [72] |
| Carbaryl | Bioelectrochemical | 300 | Well water | [72] |
| Paraaxon | Bioelectrochemical | 5.5 | Well water | [73] |
| Methyl parathion | Bioelectrochemical | 5.8 | Well water | [73] |
| Omethoate | Bioelectrochemical | 21.3 | Lake water | [74] |
| Atrazine | Bioelectrochemical | 0.15 | Drinking, lake, and agricultural wastewater | [75] |
| Isoproturon | Bio-Opt | 3 | Well water | [76] |
| Carbaryl | Bioelectrochemical | 0.029 | Drinking water | [77] |
| Carbendazim | Bioelectrochemical | 15 | Environmental water | [78] |
| Carbofuran | Bioelectrochemical | 68 | Environmental water | [78] |
| Benomyl | Bioelectrochemical | 35 | Environmental water | [78] |
| Carbaryl | Bioelectrochemical | 0.27 | River water | [79] |
| Fuberidazole | Bioelectrochemical | 0.09 | River water | [79] |
| Carbaryl | Bioelectrochemical | 6 | River, well, dam, irrigation water | [80] |
| Benomyl | Bioelectrochemical | 9 | River, well, dam, irrigation water | [80] |
| Fuberidazole | Bioelectrochemical | 0.18 | River and well water | [81] |
| O-Phenylphenol | Bioelectrochemical | 6.1 | River and well water | [81] |
| Linuron | Bioelectrochemical | 130 | Tap, underground, mineral, and river water | [82] |
| Metsulfuron methyl | Optical | 0.14 | River, well, and irrigation water | [83] |
| Analytes                      | Sensor types    | LOD (ng/ml) | Waterbodies                        | Ref.  |
|------------------------------|-----------------|-------------|------------------------------------|-------|
| α-Naphthol                   | Optical         | 2           | Tap and river water                | [84]  |
| O-Phenylphenol               | Optical         | 2           | Tap, underground, mineral, and river water | [86]  |
| Thiabendazole                | Optical         | 2           | Tap, underground, mineral, and river water | [86]  |
| Triazine                     | Biooptical      | 0.0013      | River water                        | [85]  |
| Thiabendazole                | Optical         | 2.8         | Tap, underground, mineral, and river water | [86]  |
| Warfarin                     | Optical         | 2           | River, lake, and spring water      | [87]  |
| Thiabendazole                | Optical         | 2.5         | Well, river, and irrigation water  | [88]  |
| Metsulfuron methyl           | Optical         | 3.3         | Well, river, and irrigation water  | [88]  |
| N-1-Naphthylphthlamic acid  | Optical         | 8.1         | Drinking and mineral water         | [89]  |
| 1-Naphthylamine              | Optical         | 11.2        | Tap, underground, mineral, and river water | [90]  |
| Carbaryl                     | Biooptical      | 1.38        | Groundwater, tap, and river water  | [91]  |
| 1-Naphthylamine              | Optical         | 1.1         | Tap, well, lake, river, and rain water | [93]  |
| Paraquat                     | Optical         | 0.11        | Tap, well, lake, river, and rain water | [93]  |
| Paraquat                     | Optical         | 1.6         | Wastewater                         | [94]  |
| Paraquat                     | Optical         | 0.003       | Tap, mineral, waste, and ground water | [95]  |
| Paraquat                     | Optical         | 0.7         | Drinking water                     | [96]  |
| Paraquat                     | Bioelectrochemical | 0.926     | River and groundwater              | [97]  |
| Paraquat                     | Biooptical      | 0.036       | River water                        | [98]  |
| Paraquat                     | Electronical    | 23.92       | River water                        | [99]  |
| Paraquat                     | Electronical    | 2           | Dam, river, and tap water          | [100] |
| Paraquat                     | Optical         | 22          | River, dam, and mineral water      | [101] |
| Paraquat                     | Ele-optical     | 0.1         | River water                        | [102] |
| Diquat                       | Ele-optical     | 0.2         | Tap, lake, river, ground, and bog water | [103] |
| Paraquat                     | Ele-optical     | 0.2         | Tap, lake, river, ground, and bog water | [103] |
| Diquat                       | Ele-optical     | 0.1         | Tap, lake, river, ground, and bog water | [103] |
| Paraquat                     | Ele-optical     | 5           | Tap, lake, river, ground, and bog water | [103] |
| Dipterex                     |                 | 5.152       | Tap and river water                | [106] |
| Dursban                      |                 | 7.012       | Tap and river water                | [108] |
| Paraquat                     | Che-optical     | 5.143       | Wastewater                         | [105] |
| Methyl thiophanate           |                 | 6.84        | Tap and river water                | [106] |
| Cartap                       |                 | 5.476       | Tap and river water                | [106] |
| Paraoxon                     | Optical         | 0.05        | Tap and river water                | [106] |
| Diniconazole                 | Biooptical      | 6.4         | River and wastewater               | [107] |
| Diuron                       | Electrochemical | 0.00125     | Lake water                         | [108] |
| Diazinon                     |                 | 36.3        | River water                        | [109] |
| Iprobenfos                   | Biooptical      | 53.6        | River water                        | [109] |
| Edifenphos                   |                 | 27.9        | River water                        | [109] |
| Paraoxon                     |                 | 2           | Tap and river water                | [111] |
| 2,4-D                        | Bioelectrochemical | 50        | River water                        | [110] |
| Diazinon                     | Bioelectrochemical | 0.039     | Tap and river wastewater           | [111] |
| Metamitron                   | Electrochemical | 7.28        | River water                        | [112] |
| Carbamate                    | Biooptical      | 3.3         | Lake water                         | [113] |
| Diuron                       | Bioelectrochemical | 2.1        | River water                        | [114] |
| Mesotrione                   | Electrochemical | 8.822       | Lake and tap water                 | [115] |
| Paraquat                     | Electrochemical | 3.086       | River water                        | [116] |
| Fenoxanil                    | Electronical    | 0.0092      | River water                        | [117] |
| Analytes       | Sensor types | LOD (ng/ml) | Waterbodies                      | Ref.          |
|----------------|--------------|-------------|----------------------------------|---------------|
| Malathion      | Bioelectrochemical | 0.01        | Tap and river water               | [118]         |
| Parathion methyl| Bioelectrochemical | 0.02        | Tap and river water               | [119]         |
| Monocrotophos  | Bioelectrochemical | 0.01        | Tap and lake water                | [120]         |
| Dichlorvos     |              | 0.01        | Tap and lake water                | [121]         |
| Dicloran       | Bioelectrochemical | 0.099       | Tap and river water               | [122]         |
| Fenitrothion   | Electrochemical | 0.036       | Tap and lake water                | [123]         |
| Carbamate      | Optical      | 0.023       | River water                       | [124]         |
| Fenoxycarb     | Biooptical   | 949.221     | River water                       | [125]         |
| Malathion      | Ele-optical  | 0.0991      | Pond water                        | [126]         |
| Methomyl       | Electronical | 126.192     | River and tap water               | [127]         |
| Diuron         |              | 8.1585      | Lake and well water               | [128]         |
| 2,4-D          | Electronical | 26.405      | Lake and well water               | [129]         |
| Tebuthiuron    |              | 77.625      |                                 | [130]         |
| Pyrethroids    | Biooptical   | 42.64       | River water                       | [131]         |
| 2,4-D          | Electronical | 44.008      | River water                       | [132]         |
| Fomesafen      | Electrochemical | 578         | Lake water                        | [133]         |
| Glyphosate     |              | 338         |                                 | [134]         |
| Dimethoate     |              | 458.52      |                                 | [135]         |
| Atrazine       |              | 431.36      |                                 | [136]         |
| Cyanazine      |              | 481.39      |                                 | [137]         |
| Diuron         |              | 466.2       |                                 | [138]         |
| Imidacloprid   |              | 511.32      |                                 | [139]         |
| Malathion      |              | 660.72      |                                 | [140]         |
| Imazethapyr    | Biooptical   | 578         | Lake water                        | [141]         |
| Mecoprop-P     |              | 429.3       |                                 | [142]         |
| 2,4-D          |              | 440.08      |                                 | [143]         |
| Trifluralin    |              | 670.56      |                                 | [144]         |
| Paraquat       |              | 514.32      |                                 | [145]         |
| Metolachlor    |              | 567.6       |                                 | [146]         |
| Carbaryl       |              | 402.44      |                                 | [147]         |
| Acephate       |              | 366         |                                 | [148]         |
| Dichlorophen   | Electronical | 3.768       | River water                       | [149]         |
| Hexazinone     | Bioelectrochemical | 0.00066    | River water                       | [150]         |
| Malathion      | Optical      | 1.84 × 10⁻⁷ | Agricultural runoff water and lake water | [151] |
| Fenitrothion   | Optical      | 1.677       | Well, river, and tap water        | [152]         |
| Pendimethalin  | Electronical | 10.408      | Tap and river water               | [153]         |
| Metol          |              | 0.344       | River water                       | [154]         |
| Bisphenol A    | Electrochemical | 0.685      |                                 | [155]         |
| Azinphos methyl| Che-optical  | 0.549       | Tap and river water               | [156]         |
| Fenvalerate pyrethroid | Optical | 0.01  | Tao, river, well, distilled, and draining water | [157] |
| Propham        | Electrochemical | 0.789      | River water                       | [158]         |
| Propham        | Electrochemical | 0.179      | River water                       | [159]         |
| Cyanazine      | Electrochemical | 0.06       | Tap, river, and ground water      | [160]         |
| Tau-fluvinate  | Biooptical   | 6.105       | Lake water                        | [161]         |
| Methyl parathion| Optical   | 291.3       | Lake water                        | [162]         |
| Pymetrozine    | Optical      | 2.172       | Tap and lake water                | [163]         |
| Imidacloprid   | Electronical | 106.1       | River water                       | [164]         |
| Pyrethroid     | Biooptical   | 6.568       | River water                       | [165]         |
| Paraquat       | Electronical | 0.8         | River water                       | [166]         |
| Clopyralid     | Electrochemical | 0.154      | River water                       | [167]         |
| Carbendazim    | Electronical | 37.473      | River water                       | [168]         |
2.2. Data Analysis. One-way ANOVA (analysis of variation) was conducted to test the differences of LODs among the pesticide groups/heavy metals and among the sensor types. All data were checked for normality before conducting the ANOVA tests and were log-transformed to meet normality and homogeneity assumptions [37]. One case (1.84 × 10^{-7}) was deleted from the pesticide sensor dataset due to the outlier when conducting the ANOVA. If significant effects present in the ANOVA, then Tukey’s multiple comparison was used for post hoc analysis of significant differences among sensor types or analyte groups [38]. All statistical analyses were carried out using SPSS 24.0.

3. Results and Discussion

3.1. Pesticide Sensors

3.1.1. Pesticides in Freshwaters. Pesticides are usually classified into three major categories: herbicides, insecticides, and fungicides/bactericides. The application of pesticides is used to control weeds, pest outbreaks, and fungal infestations for the security of global food supply [15, 39, 40]. The worldwide pesticide expenditures increased from $48.8 billion in 2008 to $55.9 billion in 2012 [41]. After application, these pesticides can enter freshwaters via numerous ways such as wastewater effluent and surface runoff [15]. In a national (US) monitoring network for pesticides in streams and rivers during 1992-2011, the concentrations of one or more pesticides exceeded the aquatic organism benchmark in 61%-69%, 45%, and 53%-90% of the streams in agricultural, mixed-land-use, and urban areas, respectively [42]. In Europe, atrazine (herbicide) is among the most frequently detected chemicals in groundwaters [5]. Due to their high frequency of being detected in freshwaters and the toxicity effects on aquatic organisms, pesticides are one of the most common monitored water quality parameters [43–45]. During the last few decades, many sensors have been developed to detect pesticides in freshwaters [46, 47].

Most of the sensor data we collected can be applied in rivers and streams which correspond to the fact that most studies focused on these waterbodies and indicated the needs...
to monitoring pesticides in streams and rivers. The most frequently detected pesticides are paraquat, followed by atrazine and carbyl (Table 1). This result is in accordance with the most common pesticide contamination in freshwaters [5]. However, only three studies detected glyphosate [48–50], the most widely used herbicide worldwide [51, 52]. Therefore, more studies should target on the development of glyphosate sensors to get a clearer understanding of the glyphosate contamination in freshwaters. Although the production of herbicides is the highest worldwide [53], more studies focus on insecticide sensors than herbicide sensors (Table 1), probably because organophosphorus pesticides, the most frequently detected analytes, are highly toxic to organisms [54]. Therefore, priority was given to those with relatively high toxicity rather than those used in large quantity when monitoring water quality.

3.1.2. Sensitivity of Pesticide Sensors. The average LOD of pesticide sensors included in this review was 72.53 ± 12.69 ng/ml (n = 180, mean ± SE). Not all of sensors for the detection of pesticides in freshwaters were sensitive enough for ecological and monitoring requirements. The proposed maximum contaminant level, i.e., the maximum permissible level (MCL) of a contaminant in water that is delivered to any user of a public waterbody, for many pesticides (e.g., atrazine and aldicarb) is at the level of ng/ml or even less than 1 ng/ml [170]. For example, the criterion maximum concentrations (CMC) of carbyl, chlorpyrifos, diazinon, and parathion for aquatic life in freshwaters of the United States are 2.1, 0.083, 0.17, and 0.065 ng/ml, respectively (Table 2). Moreover, more than 5% of the MCLs for the top 29 commonly regulated pesticides in drinking water exceed the computed upper thresholds for human health risk uncertainty [171], which means that the MCLs for pesticides in drinking water should be stricter and higher sensitive sensors are needed. However, our results indicated that the LODs for 32.8% of the sensors are higher than 10 ng/ml, and <50% of the sensors can reach the level of 3 ng/ml. Therefore, many sensors may not be sensitive enough for the detection of pesticides in freshwaters regarding the requirements for the protection of aquatic life and human health. In addition, there are more than 1,000 pesticides used worldwide to ensure food security. Nevertheless, this review paper only included 97 kinds of pesticides/active ingredients which cover less than 10% of all pesticides. Therefore, future studies should focus on the largely ignored pesticides because many pesticides have toxic effects on aquatic organisms [172] and human health [173, 174]. For example, many sensors were developed to analyze organophosphorus pesticides (e.g., chlorpyrifos and carbyl) while fewer sensors were targeted on organochlorine pesticides such as dichlorodiphenyltrichloroethane (DDT). DDT was widely used for the control of pest and fungus in the last century. Even though DDT has been banned for decades in many countries, it can still be found in 8–100% of the sampled small streams in three South American countries [175]. Therefore, DDT is still a global concern due to the toxicity, not easy to be degraded, and the tendency to be accumulated in organisms [176]. The LOD of one biooptical sensor used for the detection of DDT in river water can be as low as 0.015 ng/ml [177].

LODs in this study showed thousands of orders for different analytes and sensors. Among all the sensors been checked, the most sensitive sensor was developed by Kumar et al. [131], in which the indirect detection of malathion through an enzyme-based fluorometric method was applied. This system can achieve an ultrasensitive LOD which is as low as 1.84 × 10⁻⁷ ng/ml and can be spiked for lake water and agricultural runoff water [131]. By contrast, some sensors are relatively “insensitive” with the LODs at the level of 100 ng/ml [50, 122, 141]. Although, the average LOD for herbicide sensors is higher than that of insecticides and fungicides, there is no significant difference among the three categories of pesticides (F₄,176 = 2.717, P = 0.069, Figure 1). The sensitivity of sensors collected in this paper is similar to that of previous review papers [34, 178]. Only 22 cases (12.22%) were related to fungicide sensors. This extremely low percentage indicated the urgency to improve the monitoring of fungicides in freshwaters, because fungicides are widely occurring in freshwaters and are highly toxic to numerous aquatic organisms [15, 179]. For the sensor types, we found a similar pattern (Table 1) as some previous review papers that electrochemical [180], optical [33, 35], and biological [181] sensors are among the most widely used sensors for the detection of pesticides in freshwaters. Regarding the sensitivity of different types of sensors, biosensors showed

| Pesticides | CMCs (ng/ml) | MCLs (ng/ml) |
|------------|-------------|--------------|
| Carbaryl   | 2.1         | —            |
| Chlorpyrifos | 0.083     | —            |
| Diazinon   | 0.17        | —            |
| Parathion  | 0.065       | —            |
| Dieldrin   | 0.24        | —            |
| Lindane    | 0.95        | 0.2          |
| Atrazine   | —           | 3            |
| 2,4-D      | —           | 70           |
| Diquat     | —           | 20           |

| Heavy metals | CMCs (ng/ml) | MCLs (ng/ml) |
|-------------|-------------|--------------|
| Arsenic     | 340 (1.0)   | 10           |
| Cadmium     | 1.8 (1.14)  | 5            |
| Chromium³⁺  | 570 (0.316) | 50           |
| Chromium⁶⁺  | 16 (0.982)  | 50           |
| Copper      | - (0.96)    | 130          |
| Lead        | 82 (1.46)   | 15           |
| Mercury     | 1.4 (0.85)  | 2            |
| Nickel      | 470 (0.998) | —            |
| Silver      | 3.2 (0.85)  | 100          |
| Zinc        | 120 (0.978) | 500          |

Note: CMC: criterion maximum concentration for the recommended aquatic life in the United States. Numbers in parentheses of CMCs for heavy metals are conversion factors for dissolved metals. MCL: maximum contaminant limit concentration for drinking water in the United States.
the highest sensitivity compared with other sensors, while the biooptical and electrochemical optical sensors indicated the lowest sensitivity ($F_{9,169} = 7.239, P < 0.001$, Figure 2). Biosensors have been widely used in the environmental monitoring [5], given the advantages of biosensors in detecting pesticides and other pollutants over conventional methods: high stability (e.g., they can operate at high temperature), inexpensiveness, possibility for real-time monitoring, high selectivity, and disposability, just to name some of them [181–183]. Biosensors could be a promising direction for pesticide detection in freshwaters. For example, diatoms, which were popular for the assessment of water quality [184], may be a suitable tool for biosensors.

3.2. Heavy Metal Sensors

3.2.1. Heavy Metals in Freshwaters. Heavy metals refer to metallic elements that have a high atomic weight and with a
| Analytes | Sensors | LOD (ng/ml) | Waterbodies | Ref. |
|----------|---------|-------------|-------------|------|
| As⁺³⁺    | Biosensor | 0.005       | Tap, lake, and pond water | [203] |
| As⁺³⁺    | Electrochemical | 75          | River water | [204] |
| Cd⁺²⁺    | Electrochemical | 0.068       | Tap and lake water | [205] |
| Pb⁺²⁺    | Electrochemical | 0.105       | Tap and lake water | [206] |
| Pb⁺²⁺    | Optical | 0.029       | River water | [207] |
| Hg⁺²⁺    | Electrochemical | 0.044       | Tap and river water | [208] |
| Cu⁺²⁺    | Electrochemical | 9.532       | Tap and river water | [209] |
| Fe⁺³⁺    | Electrochemical | 200         | Tap and lake water | [210] |
| Ni⁺²⁺    | Electrochemical | 300         | Tap and lake water | [211] |
| Cr⁺⁶⁺    | Optical | 100         | Tap and lake water | [212] |
| Cu⁺²⁺    | Electrochemical | 30          | Tap and lake water | [213] |
| Al⁺³⁺    | Electrochemical | 80          | Tap and lake water | [214] |
| Zn⁺²⁺    | Electrochemical | 40          | Tap and lake water | [215] |
| Cd⁺²⁺    | Electrochemical | 0.337       | River water | [216] |
| Pb⁺²⁺    | Electrochemical | 0.2         | Lake water | [217] |
| Cu⁺²⁺    | Electrochemical | 0.2         | Lake water | [218] |
| Hg⁺²⁺    | Electrochemical | 0.6         | River water | [219] |
| Ag⁺⁺     | Biosensor | 0.006       | Tap, drinking, pond, and soil water | [220] |
| Cd⁺²⁺    | Electrochemical | 0.0056      | River water | [221] |
| Pb⁺²⁺    | Electrochemical | 0.0166      | River water | [222] |
| Cu⁺²⁺    | Electrochemical | 0.001       | River water | [223] |
| Hg⁺²⁺    | Electrochemical | 0.010       | River water | [224] |
| As⁺³⁺    | Electrochemical biosensor | 0.000003    | Lake and well water | [225] |
| Cd⁺²⁺    | Electrochemical | 0.17        | Lake water | [226] |
| Hg⁺²⁺    | Optical | 0.6         | Tap water | [227] |
| Pb⁺²⁺    | Electrochemical | 0.17        | River, lake, and wastewater | [228] |
| Cd⁺²⁺    | Electrochemical | 0.21        | River water | [229] |
| Hg⁺²⁺    | Electrochemical | 6.018       | River water | [230] |
| Cu⁺²⁺    | Electrochemical | 0.02        | River, tap, and well water | [231] |
| Pb⁺²⁺    | Electrochemical | 0.03        | River, tap, and well water | [232] |
| Cr⁺³⁺    | Electrochemical | 0.15        | Pond, tap, drinking, and soil water | [233] |
| Ag⁺⁺     | Electrochemical | 0.098       | Pond, tap, drinking, and soil water | [234] |
| Hg⁺²⁺    | Biofluorescent | 0.261       | Pond, tap, drinking, and soil water | [235] |
| Cd⁺²⁺    | Electrochemical | 0.05        | Tap, pond, and river water | [236] |
| Ni⁺²⁺    | Electrochemical | 0.12        | Tap and river water | [237] |
| Cu⁺²⁺    | Electrochemical | 3           | Tap and river water | [238] |
| Cd⁺²⁺    | Electrochemical | 4           | River water | [239] |
| Pb⁺²⁺    | Electrochemical | 2.5         | River water | [240] |
| Cd⁺²⁺    | Electrochemical | 1.012       | River water | [241] |
| Pb⁺²⁺    | Electrochemical | 0.207       | River water | [242] |
| Cu⁺²⁺    | Electrochemical | 0.508       | River water | [243] |
| Hg⁺²⁺    | Electrochemical | 0.181       | River water | [244] |
| Ni⁺²⁺    | Electrochemical | 240         | River water | [245] |
| Cr⁺³⁺    | Electrochemical | 180         | River water | [246] |
| Hg⁺²⁺    | Electrochemical | 190         | River water | [247] |
| Pb⁺²⁺    | Electrochemical | 0.5         | River water | [248] |
Table 3: Continued.

| Analytes | Sensors | LOD (ng/ml) | Waterbodies | Ref. |
|----------|---------|-------------|-------------|------|
| Hg2+     | Optical | 0.261       | Tap and river water | [229] |
| As3+     | Biooptical | 0.005     | Groundwater | [203] |
| Hg2+     | Biooptical | 0.241     | Lake and deionized water | [230] |
| Pb2+     | Bioelectrochemical | 0.000001  | River water | [231] |
| Cd2+     | Electrochemical | 3.372     | Lake water | [232] |
| Hg2+     | Optical | 7.422       | River water | [233] |
| Cu2+     | Electrochemical | 0.15      | Lake and river water | [234] |
| Hg2+     | Electrochemical | 0.13      | Tap and lake water | [235] |
| Cd        | Optical | 1.68        | Tap and lake water | [235] |
| Cu2+     | Optical | 1.24        | Tap and lake water | [235] |
| Pb2+     | Optical | 0.0064      | River water | [236] |
| Fe3+     | Optical | 0.056       | River water | [236] |
| Pb2+     | Biooptical | 1.036     | Lake water | [237] |
| Cd2+     | Electrochemical | 1.16      | Lake water | [238] |
| Pb2+     | Optical | 0.152       | Deionized water | [238] |
| Pb2+     | Optical | 0.216       | River and tap water | [239] |
| As3+     | Electrochemical | 0.011     | River water | [240] |
| Cd2+     | Bioelectrochemical | 2.248    | River, tap, and wastewater | [241] |
| Cd2+     | Electrochemical | 7.869     | River, tap, and wastewater | [241] |
| Pb2+     | Electrochemical | 0.5       | River water | [242] |
| Cu2+     | Electrochemical | 1         | Tap and river water | [246] |
| Cu2+     | Electrochemical | 5         | Tap and river water | [246] |
| Cr3+     | Biosensor | 0.35      | River and tap water | [243] |
| Pb2+     | Electrochemical | 4.144     | Lake and mining effluent water | [244] |
| Cd2+     | Electrochemical | 1.17      | Lake and tap water | [245] |
| Zn2+     | Electrochemical | 0.327     | Tap and river water | [246] |
| Cd2+     | Electrochemical | 0.225     | Tap and river water | [246] |
| Pb2+     | Electrochemical | 0.166     | Tap and river water | [246] |
| Cu2+     | Electrochemical | 25.418    | River, tap, and dam water | [247] |
| Cd2+     | Electrochemical | 0.0025    | River, tap, and dam water | [247] |
| Pb2+     | Electrochemical | 0.0518    | River, tap, and dam water | [247] |
| Ni2+     | Electrochemical | 0.0002    | River, tap, and dam water | [247] |
| Zn2+     | Electrochemical | 0.05      | Lake water | [249] |
| Pb2+     | Electrochemical | 0.02      | Lake water | [249] |
| Cu2+     | Electrochemical | 0.03      | Lake water | [249] |
| Pb2+     | Electrochemical | 2.486     | Tap, lake, and river water | [250] |
| Ag+      | Bioelectrochemical | 0.00000005 | Tap and lake water | [251] |
| Cd2+     | Electrochemical | 0.2       | River water | [252] |
| Pb2+     | Electrochemical | 0.3       | River water | [252] |
| Pb2+     | Electroman | 3.937     | River water | [253] |
| Hg2+     | Electrochemical | 3.611     | River water | [253] |
| Cu2+     | Electrochemical | 19.064    | Tap and river water | [254] |
| Pb2+     | Electrochemical | 192.696   | Lake water | [255] |
| Cr3+     | Optical | 48.356      | Lake water | [255] |
| Hg2+     | Optical | 186.549     | Lake water | [255] |
Aquatic ecosystems can be polluted by heavy metals through multiple ways such as mining, weathering of soils and rocks, industrial wastewater, and surface runoff [186–188]. Natural concentrations of Pb and Cd are less than 0.003 ng/ml in streams [189]. However, heavy metal concentrations may be two or three orders of the natural concentrations or even higher in polluted waterbodies [190, 191]. The most common heavy metal pollutants found in aquatic ecosystems are As, Cd, Cr, Cu, Ni, Pb, Hg, and Zn [192]. For instance, Cu, Fe,

### Table 3: Continued.

| Analytes | Sensors | LOD (ng/ml) | Waterbodies | Ref. |
|----------|---------|-------------|-------------|------|
| Cd^{2+}  | Chemical| 0.001       | Wastewater  | [256]|
| Cu^{2+}  |         | 0.006       |             |      |
| Hg^{2+}  |         | 0.020       |             |      |
| Pb^{2+}  |         | 0.021       |             |      |
| Mn^{2+}  |         | 16          |             |      |
| Fe^{3+}  | Optical | 11          | River water | [257]|
| Cu^{2+}  |         | 12          |             |      |
| Fe^{3+}  |         | 50          |             |      |
| Hg^{2+}  | Optical | 0.233       | River and tap water | [258]|
| Hg^{2+}  |         | 0.509       |             |      |
| Hg^{2+}  | Biooptical | 0.602       | Lake water  | [259]|
| Ag^{+}   |         | 0.324       |             |      |
| Cd^{2+}  | Optical-electrochemical | 0.152       | River water | [260]|
| Pb^{2+}  |         | 0.029       |             |      |
| Cd^{2+}  |         | 0.315       | River and tap water | [261]|
| Pb^{2+}  | Electrochemical | 0.292       |             |      |
| As^{3+}  |         | 0.172       |             |      |
| Hg^{2+}  |         | 0.321       |             |      |
| Cu^{2+}  | Biooptical | 5547.566    | Pond wand tap water | [262]|

**Figure 3:** Averages of limit of detection of sensors for the detection of heavy metals in freshwaters. Values are the mean ± SE. Different uppercase letters above each bar indicate significant differences after one-way ANOVA and post hoc Tukey (parameters with the same letter are not significantly different between heavy metal sensors). Only one sensor was included in this review for the detection of Al, Mn, and Fe. Therefore, these three heavy metal sensors were excluded from the ANOVA. The data of Cr^{3+} and Cr^{6+} were combined for the ANOVA.
Zn, Mn, and Cr were the top five heavy metals of concern in freshwaters in Bohai Region, China, while Hg showed the lowest risk [193]. The concentrations of many heavy metals in the river Ganga water and sediment exceeded the acceptable concentrations and threatened human health and aquatic organisms [194]. Three countries, i.e., the United States, Germany, and Russia, consume 3/4 of the world’s most widely used metals. Human health and aquatic ecosystems can be threatened by heavy metals especially by Pb, Cd, Hg, and As [195, 196]. For example, groundwaters contaminated by As threatened millions of people’s drinking water safety in developing countries such as India, Cambodia, and Vietnam [4]. Aquatic organisms still suffer from the toxic effects of heavy metals even though upstream mining activities ceased for decades [197]. Due to the high toxicity and them commonly found in freshwaters [198, 199], heavy metals are among the most important indices when monitoring water quality [45, 200].

3.2.2. Sensitivity of Heavy Metal Sensors. Altogether, 61 publications were selected during the years 2017-2019 (the data were updated until October 2019), with nine types of sensors used for the detection of 13 heavy metals in freshwaters (Table 3). The average LOD for all sensors is $65.36 \pm 47.51$ ng/ml ($n = 117$, mean ± SE). The sensitivity of sensors differed among the detected heavy metals ($F_{9,104} = 2.289$, $P = 0.022$, Figure 3). Sensors targeted on Ag had the highest sensitivity while the sensors used to detect Fe and Cr showed the lowest sensitivity. The sensitivity of many sensors can satisfy the requirements for drinking water and wild life protection. The LODs of some sensors were still higher than CMCs or MCLs. Especially for mercury sensors, 30% of the collected sensors failed to satisfy the CMC or MCL requirements. It reminds us that higher sensitivity sensors should be developed to protect human health and aquatic organisms. In addition, the CMC/MCL may be changed due to the national regulation [201, 202] which means that the higher sensitivity sensors may be needed to detect lower concentrations of heavy metals. As mentioned above, As, Cr, Ni, and Zn are among the highest concentrations of heavy metals in freshwaters [192]. However, limited sensors were developed to detect these heavy metals. Therefore, more diverse sensors should be developed to analyze these heavy metals.

Regarding the sensor types, more than half of the heavy metal sensors were based on electrochemical methods, while few studies applied biological ways (Table 3). The sensitivity of sensors for heavy metal detection varied among sensor types ($F_{8,108} = 12.5$, $P < 0.001$, Figure 4). Bioelectrochemical sensors had the highest sensitivity, while bioelectronical sensors showed the lowest sensitivity. The most sensitive sensor was a bioelectrochemical sensor which was developed by Zhang et al. [251] for the detection of silver in tap and lake water, and the LOD was as low as $5.0 \times 10^{-5}$ ng/ml. On the contrary, a pigment-based whole-cell biosensor developed for the analysis of copper in pond and tap water showed the highest LOD (5547.6 ng/ml) [262]. The average LOD of heavy metals based on electrochemical methods was $12.187 \pm 5.446$ ng/ml ($n = 65$, mean ± SE). The LOD of
electrochemical sensors in this review is higher than the LODs of electrochemical sensors in previous review papers [210, 263, 264]. This probably is because the LODs of four electrochemical sensors were higher than 50 ng/ml which increased the average LOD. Electrochemical sensors have the advantages such as easy to manipulate, cheap, suitable for field monitoring, and portable which make it suitable for heavy metal detection [263]. However, the optical sensors in this review did not show higher sensitivity than electrochemical sensors as mentioned in a previous study [263]. This is caused by two studies which used colorimetric and luminescent detection; the LODs in these two studies are 30-300 ng/ml [209, 255].

4. Conclusion

This review presents the general information on sensors for the detection of pesticides and heavy metals in freshwaters. The studied sensors covered less than 10% of all registered pesticides/ingredients. Most of the selected pesticide sensors were used to analyze insecticides and herbicides while limited studies were focused on fungicides. The LODs of ~30% of the pesticide sensors failed to meet the maximum permissible concentrations for aquatic life and drinking water. Biosensors showed the highest sensitivity and appeared to be a promising technology in future development for the detection of pesticides in freshwaters. The average LOD of sensors for the detection of heavy metals is 65.36 ng/ml during the last three years. The LODs of a small fraction of sensors such as mercury sensors were higher than the upper threshold concentrations for the protection of wild life and drinking water safety. Most of the heavy metal sensors were designed to detect mercury, cadmium, lead, and copper based on electrochemical methods. These results imply us that higher sensitivity sensors should be developed in the future. In addition, future sensors should cover more pesticides and heavy metals (e.g., glyphosate and zinc) which are commonly detected in waterbodies and are highly toxic to aquatic organisms and human health.

Conflicts of Interest

The authors declare that there is no conflict of interest regarding the publication of this paper.

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