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Occurrence and Distribution of Neonicotinoid Pesticides in Chinese Waterways: A Review

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Abstract: Neonicotinoid pesticides (NEOs) were initially considered viable alternatives to conventional organo-pesticides extensively used in agriculture, horticulture, and households. However, the increased frequency and concentration of NEOs in waterways have drawn significant attention and concern due to the resulting threats to ecosystems and public health worldwide. The demand for monitoring NEOs in water has led to numerous efforts in many countries and regions. Given occurrence and distribution of these pesticides/insecticides. This study reviews NEOs monitoring in China from 2019 to 2022, aiming to gather and analyse information on China's efforts in NEOs monitoring to provide reference for future research. The study primarily focuses on the southern and southeastern regions of China, specifically on lakes and tributaries of rivers, including Taihu Lake, Pearl River, Yangtze River, Songhua River, and Liao River. This focus can be attributed to the prioritisation and environmental demands related to the local economic status and major developmental tasks. The evaluation of the corresponding ecological risks of human exposure to NEOs ranged from low to medium-high levels. However, despite these findings, contamination from NEOs is still considered to lack sufficient attention and concern. Additionally, the presence of NEOs in other environmental media, such as indoor dust, wheat grains, vegetables, and teas, requires close attention in the future.

Keywords: ecological risk; neonicotinoid pesticides (NEOs) occurrence; public health; water contaminant monitoring

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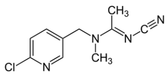
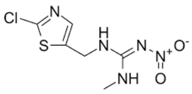
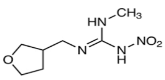
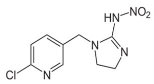
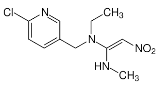
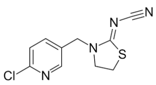
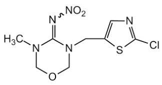
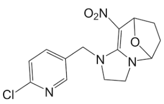
1. Introduction

Aside from the application of protective agent-type pesticides, systemic pesticides have been introduced. These pesticides can systematically travel through plant tissues and protect all parts of the crops. They assist in inhibiting sucking insects and some chewing insects, such as termites and grubs, and are widely applied as seed treatments [1–5]. Due to the phasing out of conventional organochlorine pesticides, as mandated by the Stockholm Convention, a range of alternatives to existing pesticides has emerged in the market and is currently in use [6]. Neonicotinoid pesticides (NEOs) have been introduced in practice as replacements for organochlorine and organophosphorus pesticides. Specifically, NEOs mainly act as agonists at the nicotinic acetyl-choline receptor of insects, which is the Na^+/K^+ ionophore managing the initiation of the electric signal in the postsynaptic neuron [7]. As a result, NEOs contribute to pest inhibition in both agricultural and garden settings [3,4]. Additionally, neonicotinoid pesticides are less toxic to non-target invertebrate species and potentially honeybees in comparison to conventional organo-sulphur, organochlorine, and organophosphate pesticides [8]. Because of their aforementioned beneficial properties, neonicotinoids have found extensive use in agriculture, horticulture, and household applications [9]. The currently popular NEOs include, but are not limited to, acetamiprid, clothianidin, dinotefuran, imidacloprid, and thiamethoxam, and newer NEOs species were recently developed and introduced, such as cycloxaprid and paichongding [10,11]. Table 1 lists the typical neonicotinoids that demonstrate the chemical structures and basic properties of NEOs.

Imidacloprid is one of the common types of NEOs, which was developed in the 1980s and has been available on the market since the early 1990s [8]. Subsequently, the demand for imidacloprid has been consistently rising. It has been registered in over 120 countries and, since 2014, has constituted more than a quarter of the insecticide market [12]. Specifically, China, being the main supplier of imidacloprid in the world, produced more than 23,000 tons of imidacloprid in 2016.

Table 1. Basic chemical and physical properties of neonicotinoids.

Neonicotinoids	Chemical Structure	CAS No.	Molecular Mass (g moL^{-1})	PKa	LogK$_{ows}$	Water Solubility (mg L^{-1})	Water-Sediment Photolysis (DT$_{50}$ in days)	Water Photolysis (DT$_{50}$ in days)	Water Hydrolysis (DT$_{50}$ in days)	References
■ Acetamiprid		135410-20-7	222.678	0.7	0.8	2950	4.7 (moderatly fast)	34 (stable)	420 (stable)	[13,14]
■ Clothianidin		210880-82-5	249.67	11.1	0.905	327	41–56 (stable)	<1; 0.1 (fast)	14.4 (moderately fast)	[13,14]
■ Dinotefuran		165252-70-0	202.214	12.6	−0.549	39,830	n.a.	0.2 (fast)	n.a. (stable)	[13,14]
■ Imidacloprid		80-09-1	255.661	8.00	0.57	0.58–0.61	30–129 (slow to stable)	<1, 0.2 (fast)	>365 (stable)	[13,14]
■ Nitenpyram		150824-47-8	270.72	3.1	−0.66	570,000	n.a.	n.a.	Stable at pH3–7 Fast at pH9	[13,14]
■ Thiacloprid		111988-49-9	252.72	n.a.	1.26	184	8–28 (stable)	10–63 (stable)	n.a. (stable)	[13,14]
■ Thiamethoxam		153719-23-4	291.71	n.a.	−0.13	4.1	31–40 (stable)	2.7–39.5 (moderately fast)	11.5 (stable)	[13,14]
■ Cycloxaprid		1203791-41-6	322.75	3.42	n.a.	1616.19	n.a.	n.a.	n.a.	[15]

However, NEOs pose threats to human health and ecological security. Iturburu and colleagues reported that NEOs such as imidacloprid can cause DNA damage in fish tissue [16]. Other studies have shown that communities' terrestrial invertebrates such as ants, dragonflies, and mayflies could be damaged and social behaviour can be changed in ants due to exposure to NEOs [17,18]. Additionally, the embryotoxicity of thiacloprid to mice and rabbits was proven [19,20]. Between 1994 and 2011, the detection rate of NEOs in the urine of Japanese women increased significantly [21], and it was discussed that exposure and long-term accumulation of NEOs in the human body may pose a potential endocrine disruption risk to human health. Additionally, it was reported that children with prenatal exposure to imidacloprid had a slightly higher rate of autism disorder (ASD) than the control group [22]. Also, Chen and colleagues found that continued exposure to NEOs can lead to cardiovascular effects, mental disorders, and neurodegenerative diseases, because the increased concentration of NEOs is most likely to affect target lipids and fat in tissues and cells [23]. Moreover, Zhang's team also reported that NEOs were frequently detected in the teeth and the relevance between the exposure to NEOs and periodontitis [24].

Neonicotinoid pesticides have high water solubility and a long half-life in soil, and they can easily be transported to surface waters [25,26]. Thus, NEOs and the corresponding ecological risks have been reported in developed countries and regions such as the United States, Canada, Japan, and the European Union [25].

According to the previous studies, emerging neonicotinoid pesticides (NEOs) have been continuously detected in water bodies in different countries and regions throughout the year [27,28]. NEOs ranging from 10 to 1000 ng L^{-1} have been reported in the Netherlands, Spain, Canada, and the United States [5]. As high as 10 μg L^{-1} and 100 μg L^{-1} of nicotinic insecticides have been reported in some urban suburbs and remote rural areas in the Eastern United States and Canada. Such high concentrations pose a significant and serious threat to local bee and bird populations [29]. The highest levels of NEOs were found in the Netherlands, where concentrations of imidacloprid were detected in surface water ranging from 0.001 to 320 μg L^{-1} [30–32], which is much higher than the standard set by the Dutch government [32]. In addition to the contamination detected in the raw water source, the levels of imidacloprid detected in the finished water extracted from the water treatment plant are also of interest to researchers [33]. Some studies have found that the concentration of NEOs (e.g., imidacloprid) in treated drinking water can still reach up to 240 μg L^{-1}, which is consistent with that in surface water near the water treatment plants [34]. In 2018, Napierska and colleagues highlighted that neonicotinoids (imidacloprid, thiacloprid, thiamethoxam, clothianidin, and acetamiprid) had been listed on the Watch List under the Water Directive of the European Commission for further monitoring [35].

In 2013, the use of clothianidin, imidacloprid, and thiamethoxam for seed treatment was restricted, and in 2018, the outdoor use of these NEOs was phased out by the EU Commission [35,36]. Additionally, in Canada, nationwide restrictions have been implemented to protect aquatic species and honeybees by limiting the use of clothianidin, imidacloprid, and thiamethoxam [37]. Due to the frequent observation of the ecological risks [33], the USA implemented restrictions on the use of clothianidin, imidacloprid, and thiamethoxam, while France enacted a ban on acetamiprid (ACE) and thiacloprid (THA) [35,38].

A total of 173 relevant studies on monitoring NEOs concentrations were conducted in 120 countries between 1998 and 2022. These studies found that the detection frequency of NEOs was notably high in developed countries, including the USA, Canada, the EU, and Japan [39]. In the USA, concentrations of acetamiprid, clothianidin, imidacloprid, and thiamethoxam ranged from 8 to 202 ng L^{-1}. Between 2004 and 2011, the detection trends for imidacloprid increased in both finished and untreated water samples [40].

A monitoring study conducted on 38 streams in the USA between 2012 and 2014 revealed concentration ranges of thiamethoxam, imidacloprid, acetamiprid, and clothianidin of 0–190 ng L^{-1}, 0–142 ng L^{-1}, and 0–45.6 ng L^{-1}, respectively [27]. In the selected Canadian watersheds in 2016, the concentrations for thiamethoxam, imidacloprid, acetamiprid, and clothianidin reached very high levels, ranging from n.d. to 1607 ng L^{-1}, n.d. to 1333 ng L^{-1}, n.d. to 109 ng L^{-1}, and n.d. to 778 ng L^{-1} [41].

Eight downstream areas of rivers and estuaries in the Indramayu Regency found high detection frequencies of imidacloprid and thiamethoxam, reaching levels of 75% and 62.5%, with mean concentrations of 8.75 and 7.13 ng L^{-1}, between November 2020 and August 2021 [42]. During 2009–2010, the median concentrations of thiamethoxam, imidacloprid, acetamiprid, and clothianidin were 2.65, 5.55, 1.4, and 3.2 ng L^{-1}, respectively, in Osaka rivers of Japan [43].

Moreover, it was noted that imidacloprid and thiamethoxam were frequently detected in watersheds, with concentration ranges of 5 ng L^{-1} to 43 ng L^{-1} and 6 ng L^{-1} to 43 ng L^{-1}, respectively, in seven sampling campaigns in Poland from 2017 to 2018 [44].

Due to the numerous monitoring studies having been conducted, the maximum impact concentrations (MICs) of neonicotinoid are available in approximately 93% of the global agricultural areas [39]. Among the obtained MICs, 96.7% were sampled from freshwater systems, while the MICs of neonicotinoids in estuaries were scarce [39].

Neonicotinoid pesticides (NEOs) possess threats to ecology and human heath globally, and China has been conducting similar investigations, covering lakes, rivers, and tributaries near agricultural regions in the northeast and the south [13,45,46]. These studies not only monitor the presence and distribution of NEOs but also provide insights into the corresponding ecological and human exposure risks in these regions. However, public attention and concern regarding this matter remain insufficient, highlighting the pressing need to bridge this knowledge gap and implement potential environmental management strategies [6]. In response to this situation, this study mainly focuses on the NEOs monitoring cases in China and reviews and synthesises these Chinese studies to raise public awareness and concerns about the occurrence of NEOs and the resulting potential health and ecological risks.

2. Analytical Methods and Regulations for Neonicotinoid Pesticides

2.1. Multiple National Regulations

The USEPA proposed an interim decision for managing the use of acetamiprid, clothianidin, dinotefuran, imidacloprid, and thiamethoxam. This proposal involves reducing the amount of neonicotinoid pesticides (NEOs) used on crops associated with ecological risk, implementing requirements for personal protective equipment to minimise occupational risks, and placing restrictions on applying NEOs to blooming crops to limit exposure to bees and birds. Additionally, there is an effort to educate homeowners about using fewer NEOs and a plan to phase out NEOs applications on residential turfs [47].

The initial regulatory action concerning the use of imidacloprid, clothianidin, and thiamethoxam in seed coating and other outdoor applications was introduced in Europe in 2013 (EC485/2013) [36,48]. Subsequently, these restrictions were reinforced in 2018 to limit the marketing authorisation of imidacloprid, clothianidin, and thiamethoxam through Commission Implemented Regulations 2018/783, 2018/784, and 2018/785 [36,48]. However, in the third version of the EU Watch List (EU 2020/1161), NEOs were not listed, and certain countries, including Austria, Belgium, Croatia, Denmark, Finland, France, Lithuania, Poland, Romania, Slovakia, and Spain, have permitted the 'emergency use' of banned neonicotinoids for major crops, particularly in seed coating for sugar beets [49]. Nevertheless, the regulatory and restriction efforts persist from EC countries; for instance, the renewal of the approval of thiacloprid was rejected, aligning with the scientific advice provided by the European Food Safety Authority (EFSA), which highlights the substantial health and environmental concerns associated with NEOs [36,48].

The Canada Council reported that NEOs, such as imidacloprid, could pose ecological risks to local honeybee and bird communities. The Canadian Pest Management Regulatory Agency (PMRA) published their final pollinator re-evaluation decisions for the three registered NEOs in Canada, banning some other NEOs applications and implementing mitigation measures. In 1999, France banned the application of neonicotinoids on sunflowers and, in 2004, on corn [38]. The application of thiamethoxam on rapeseed has also been restricted since 2012. In 2016, the French government adopted a bill to ban the application of NEOs in plant protection, which was implemented in 2018 [38]. The Netherlands also regulated the use of imidacloprid, setting an Annual Average Environmental Quality Standard (AA-EQS) of 0.067 $\mu g\ L^{-1}$ and a maximum acceptable concentration environmental quality standard (MAC-EQS) of 0.2 $\mu g\ L^{-1}$ [31]. While the UK had previously approved the use of five NEOs, only acetamiprid currently has approval for use, following the EC's updated regulations in 2018 [50]. Australia has recently taken action to assess the environmental risk of NEOs on non-target species and minimise the potential risks by specifying use patterns and safety directions [51]. In 2019, the Australian Pesticides and Veterinary Medicines Authority (APVMA) initiated a review process to assess approved active constituents and products containing neonicotinoids. This review aimed to ensure compliance with safety standards related to both human health and ecological security [52]. The regulatory threshold levels (RTLs) for these five countries/regions are listed in Table 2. It is important to note that the regulation of NEOs has not yet commenced in most parts of the world, especially in developing countries.

In China, the maximum residual levels (MRLs) of NEOs in agricultural products are established; the MRLs of acetamiprid, clothianidin, and thiacloprid are 2 $mg\ kg^{-1}$, 0.4 mg kg^{-1}, and 0.7 mg kg^{-1}, respectively. Based on the toxicity reference value from the combined results of the Hazard Quotients (HQs) method and Probabilistic Risk Assessment (PRA), one study proposed regulatory values of the surface water quality of NEOs in China: acetamiprid, 0.04 μg L^{-1}; clothianidin, 0.22 μg L^{-1}; imidacloprid, 0.01 μg L^{-1}; and thiamethoxam, 0.24 μg L^{-1} [53]. However, China currently lacks water quality criteria (WQC) of neonicotinoids, though the Netherlands, Germany, the USA, and Canada have established water quality guidelines (WQGs) or WQC for NEOs. Li (2023) reported that there are no WQC for IMI, which is one of the commonly used NEOs. It was also highlighted by Chen (2019) that the safety use and monitoring studies of NEOs are very scarce [54,55]. In view of the above statements, the monitoring studies of NEOs in China are in high demand to provide further referential information and for the establishment of WQC of NEOs in China.

Table 2. Regulatory threshold levels of NEOs in different countries.

Countries	RTL (μg L^{-1})	Acetamiprid	Clothianidin	Dinotefuran	Imidacloprid	Thiacloprid	Thiamethoxam	References
EU	Short-term Long-term	0.3667 0.3667	3.1 3.1	n.a. [1] n.a.	0.098 0.009	0.0912 0.45	0.14 1	[39]
USA	Short-term Long-term	1.6555 0.36	1.77 0.05	4.915 3.1	0.0385 0.01	18.9 0.97	3.535 0.74	[39]
Canada	Short-term Long-term	12 5000	1.3 0.12	n.a. n.a.	0.54 0.16	20.35 0.68	9 3	[39]
Netherland	Short-term Long-term	n.a. n.a.	n.a. n.a.	n.a. n.a.	0.067 0.2	n.a. n.a.	n.a. n.a.	[31]
Germany	Short-term Long-term	n.a. n.a.	n.a. n.a.	n.a. n.a.	0.0024 0.1	n.a. n.a.	n.a. n.a.	[56]

[1] Indicates not available.

2.2. Analytical Methods of NEOs in Surface Water and Drinking Water

It is crucial that most monitoring studies involve the establishment of analytical methodologies for neonicotinoids, encompassing both the parent compounds and derivative metabolites/by-products. Sample pretreatment is especially important due to the complexity of matrices and the low concentrations of residual analytes [57].

Solid-phase extraction (SPE) stands as one of the most popular methods for sample pretreatment, involving the extraction of target analytes and the removal of complex matrices. The advantages of SPE include high enrichment factors, flexible sorbent selection, ease of use, and speed. This technique has found wide applications in extracting neonicotinoid insecticides from various environmental and human metabolic media, such as water, soil, sediments, dust, food, vegetables, blood, urine, and plasma. Over time, various novel SPE techniques have been introduced in analytical experiments, such as dSPE, MSPE, MSPD, and SPME. Consequently, SPE has become a prevalent technique for isolating neonicotinoid insecticides from complex matrices [57,58].

Regarding the analytical apparatus, high-performance liquid chromatography (HPLC) coupled with mass spectrometry (MS), HPLC-MS, is the prevalent technique for simultaneously detecting multiple neonicotinoids and their metabolites. Currently, this method has evolved into different detection techniques, including UV, DAD, MS, immunoassay, optical, and electrochemical methods [58].

The recorded methods in Tables 3 and 4 are those adopted for various neonicotinoid pesticides (NEOs) monitoring in the Chinese studies considered. It can be seen that the primary approaches for analysing NEOs in surface water and drinking water are SPE and HPLC-MS (Tables 3 and 4). However, it is worth noting that the liquid–liquid extraction method could also serve as a viable sample pretreatment technique [59]. In most mainstream studies, water samples are initially collected and subsequently analysed in the laboratory. The introduction of the Polar Organic Chemical Integrative Sampler for on-site collection and NEOs extraction in surface water represents a novel avenue for future monitoring studies. The utilisation of isotope internal standards was a common practice to ensure the accuracy of measurements in the reported studies.

Table 3. Surface water sample pretreatment and analytical methods in the reported studies.

Site/Location (China)	NEOs	Extraction	Analytical Device	References
Taihu Lake, Wujin, Jiangsu (*n* = 316)	Acetamiprid Imidacloprid	Filtration through fibreglass filter and pH adjusted to 3 SPE Extraction: • PEP-SPE column (Bona-Agela Technologies, Tianjin, China) • Condition: 5 mL MeOH, 5 mL ultrapure water and 5 mL HCl (pH3) • Wash: added 4 mL ultrapure water • Loading: added 200 water sample • Elusion: added 3 mL MeOH (x2) • Nitrogen blowing and re-dissolve in 0.5 mL $MeOH/H_2O$ (v/v, 1/1)	HPLC-ESI-MS/MS: • Ultimate 3000 HPLC system, Dionex, USA • Agilent XDB C18 column (150 mm ×3.0 mm) • electrospray ionisation tandem mass spectrometry).	[45]
Taihu Lake, Jiangsu (*n* = 208)	Acetamiprid Clothianidin Imidacloprid Thiamethoxam	Filtration by 0.45 µm fibreglass filter pH adjusted to 3 Isotopically labelled internal standards (ILIS) added in water samples (final ILIS conc.: 50 ng L^{-1}) Online SPE coupled with LC-ESI-MS/MS • PLRP-s SPE column • Loading: added 1.8 mL aqueous sample • 1.8 mL $MeOH/H_2O$ (0.05% formic acids) at a volume ratio of 98:2 at 1.5 mL min^{-1}.	HPLC-ESI-MS/MS • Agilent 1260 series LC system • Agilent Eclipse Plus C18 column (2.1 × 150 mm, 3.5 µm) • 1290 infinitely II in line filter (0.3 µm) • Agilent 6470 triple quadrupole mass spectrometer with Jet Stream electrospray ionisation source	[39]
Pearl River Guangdong (*n* = 66)		14-day on-site capture and extraction of NEOs by the POCIS devices. • Rinse retrieved POCIS was rinsed with ultrapure water to remove solid debris • POCIS sorbents was transferred to the 6 mL cartridge and vacuum dried for 15 min • Loading: added surrogate and acetamiprid-d_3 (1 µg mL^{-1}, 50 µL). • Elusion: 10 mL acetonitrile and nitrogen blowing dried • Reconstituted to 0.5 mL and imidacloprid-d_4 (1 µg mL^{-1}, 50 µL) as the internal standard • Filtrated through a 0.22 µm filter.	HPLC-MS/MS • LC-30-AD HPLC (Shimadzu, Japan) • Agilent eclipse plus C18 column (100 mm × 2.1 mm × 1.8 µm) coupled with C18 guard column (12.5 mm × 2.1 mm × 5 µm) • QTRAP 5500MS/MS (AB SCIEX, USA) with electrospray ion source.	[25]
Pearl River Guangdong (*n* = 85)	Acetamiprid Clothianidin Imidacloprid Thiacloprid Thiamethoxam	Filtration of water sample through 0.45 µm filter Spiking of internal standards mixture (10 ng/500 mL) in filtered samples. SPE extraction: • Poy-Sery HLB SPE cartridge (500 mg, 6 mL) • Loading: loaded 500 mL water sample at 3 mL min^{-1} • Elusion: added 5 mL of Milli-Q water and MeOH • Nitrogen blowing dried and reconcentrated in 0.5 mL acetonitrile.	Triple quadruple LC_MS/MS (TSQ quantum ultra, Thermo Scientific, USA) • Thermo Hypersil GOLD C18 column (2.1 mm × 100 mm, 1.9 µm, Thermo, USA) • Electrospray ionisation positive mode	[60]
Pearl River, Guangzhou (*n* = 14)	Acetamiprid Clothianidin Imidacloprid Thiacloprid Thiamethoxam	Filtration of water sample through 0.45µm filter and spiked with internal standards mixture. SPE extraction: • Poy-Sery HLB SPE cartridge (500 mg, 6 mL) • Loading: loaded 500 mL samples • Elusion: added 5 mL of Milli-Q water and MeOH • Nitrogen gas blowing dried and reconcentrated in 0.5 mL acetonitrile	Triple quadruple LC_MS/MS (TSQ quantum ultra, Thermo Scientific, USA) • Thermo Hypersil GOLD C18 column (2.1 mm × 100 mm, 1.9 µm, Thermo, USA) • Electrospray ionisation positive mode	[13]

Table 3. *Cont.*

Site/Location (China)	NEOs	Extraction	Analytical Device	References
Central Yangtze River from Zhijiang to Wuhan (n = 120)	Acetamiprid Clothianidin Imidacloprid Nitenpyram Thiacloprid Thiamethoxam	Spiking of 20 ng of the imidacloprid-*d4* into each water sample and filtered through a glass fibre filter. SPE extraction: • HLP column (500 mg, 6 mL, Waters, Milford, MA, USA) • Condition: added 5 mL of MeOH • Loading: added 1000 mL water sample and dried cartridge • Elusion: added 100 mL MeOH • Nitrogen blowing dried and reconcentrated in 1 mL of 60% acetonitrile in water.	UPLC-MS/MS • Water Xevo TQS triple quadrupole mass spectrometry • ACQUITY I-Class UPLC (Waters Corporation, Milford, MA, USA) • ACQUITY UPLC HSS T3 column (100 mm × 2.1 mm, 1.8 µm, Waters Corporation, Milford, MA, USA).	[46]
Yangtze River Wuhan (n = 14)	Acetamiprid Clothianidin Dinotefuran Desmethyl-acet-amiprid Imidacloprid Nitenpyram Thiacloprid Thiamethoxam	Filtration of water sample and spiked isotope-labelled mixed internal standards (100 µL of 100 ng mL^{-1}) in 1 L water sample SPE extraction: Oasis HLB column (6 cc/500 mg, 60 µm, Waters Corporation, Milford, MA, USA) • Condition and dried: added 5 mL LC-MS grade acetonitrile • Rinse: added 5 mL LC-MS grade water • Loading: added 1000 mL sample in column • Wash: add 5 mL water and vacuum dried cartridge • Elusion: added 6 mL of acetonitrile • Nitrogen dried elutes and reconstituted in 1 mL 50% acetonitrile	UPLC-MS/MS • Water Xevo TQS triple quadrupole mass spectrometry • ACQUITY I-Class UPLC (Waters Corporation, Milford, MA, USA) • ACQUITY UPLC HSS T3 column (100 mm × 2.1 mm, 1.8 µm, Waters Corporation, Milford, MA, USA).	[61]
Han River Wuhan (n = 6)	Acetamiprid Clothianidin Dinotefuran Desmethyl-acet-amiprid Imidacloprid Nitenpyram Thiacloprid Thiamethoxam			
Rivers surrounding Bohai Sea (summer) (n = 72)	Acetamiprid Clothianidin Desnitro-im-imdacloprid Dinotefuran Fipronil Fipronil-desulfi-nyl Fipronil-sulphide Fipronil-sulfone Imidacloprid Thiacloprid Thiamethoxam	Water sample filtered and spiked with 20µL IS-mix (0.4 ng L^{-1}) Automated SPE extraction • Automated SPE device: LC-Tech FREESTYLE^{TM} XANA workbench (LC-Tech GmbH, Germany) • Oasis HLB cartridges (6 cc, 500 mg, 60 µm, Waters, USA) • Condition: added 10 mL MeOH • Equilibration: 10 mL ultrapure water • Loading at 8 mL min^{-1} and dried cartridge afterwards for 60 min • Elusion: added 10 mL MeOH • Eluate was dried to 0.8 mL and filtered through cellulose filter, 100 µL filtrate was collected and diluted with 0.4 mL MeOH and 0.5 mL ultrapure water.	HPLC-MS/MS • Agilent 1290 HPLC system • Zorbax Eclipse XDB-C18 (2.1 × 150 mm, 3.5 µm, Agilent, Germany) combined with a Zorbax Eclipse XDB-C18 guard column (2.1 × 5 mm, 1.8 µm, Agilent, Germany) • Agilent 6490 triple quadrupole mass spectrometry with Agilent Jet Stream electrospray ionisation (ESI) source	[62]
Bohai Sea water (summer) (n = 81)	Acetamiprid Desnitro-im-imdacloprid Fipronil Fipronil-desulfi-nyl Thiacloprid			
Songhua River, Harbin (n = 13)	Acetamiprid Clothianidin Dinotefuran Imidacloprid Imidaclothiz Thiacloprid Thiamethoxam	Water samples were filtered through a Teflon filter and spiked with a mixed internal standards mixture (50 µL of 1 mg L^{-1}) SPE extraction: • Water Oasis HLB cartridge (500 mg, 6 cc, Milford, MA, USA) • Pre-condition: 5 mL MeOH and 5 mL ultra-pure water • Loading water samples and air dried the cartridge • Elution: added 5 mL ultra-pure water in cartridge • Eluents were nitrogen blowing dried then reconstituted in 1 mL 25% acetonitrile in water and filtered through the 0.22 µm filter.	LC-MS/MS • AB SCIEX triple Quad 500 HPLC-MS/MS (Framingham, MA, USA) • Phenomenex Kinetex C18 column (100 mm × 2.1 mm, 1.7 µm). • Electrospray ionisation source in postie ion mode with multiple reactions monitoring mode.	[63]

Table 4. Drinking water sample pretreatment and analytical methods in the reported studies.

Site/Location	NEOs	Extraction	Analytical Device	References
Wuhan (*n* = 165)	Acetamiprid Clothianidin Dinotefuran Desmethyl-acetamiprid Imidacloprid Nitenpyram Thiacloprid Thiamethoxam	Filtration of water sample and spiked isotope-labelled mixed internal standards (100 µL of 100 ng/mL) in 1 L water sample SPE extraction: • Oasis HLB column (6 cc/500 mg, 60 µm, Waters Corporation, Milford, MA, USA) • Condition and dried: added 5 mL LC-MS grade acetonitrile • Rinse: added 5 mL LC-MS grade water • Loading: added 1000 mL sample in column • Wash: added 5 mL water and vacuum dried cartridge • Elusion: added 6 mL acetonitrile Nitrogen dried elutes and reconstituted in 1 mL 50% acetonitrile	UPLC-MS/MS • Water Xevo TQS triple quadrupole mass spectrometry • ACQUITY I-Class UPLC (Waters Corporation, Milford, MA, USA) ACQUITY UPLC HSS T3 column (100 mm × 2.1 mm, 1.8 µm, Waters Corporation, Mildford, MA, USA).	[61]
Hangzhou (*n* = 71)	Acetamiprid Clothianidin Dinotefuran Imidacloprid Nitenpyram	Liquid–liquid extraction: • Added 2 g NaCl and 25 µL of surrogate standards (IMI-d_4, THI-d_3) to 50 mL of each water sample and shaken for 10 s • Added 30 mL of dichloromethane and shaken for 6 min • Organic phase was removed and eluted by passing the sample through a chromatographic column (8 g of anhydrous sodium sulphate) • Eluted aliquot was dried by rotary evaporator and reconstituted in 2 mL acetonitrile and then vortexed for 1 min, this led to the concentration factor of 25 for the original levels in water samples • 40 µL of internal standard CLO-d_3 was added and final solution was stored at −20 °C for later analysis.	UPLC-MS/MS (UPLC-MS/MS, Waters Corporation, Milford, MA.) • YMC ODS-AQ chromatography column (100 mm × 2.1 mm, 3 µm, YMC, Allentown, PA, USA) • Triple quadrupole mass spectrometer Xevo TQ-S (Waters Corporation).	[59]
Nationwide (*n* = 84)	Acetamiprid Clothianidin Dinotefuran Imidacloprid Thiacloprid Thiamethoxam	Water samples were spiked with mixed isotope internal standard solution (50 µL, 0.1 ng µL^{-1}) and then filtered through 0.45 filter. SPE extraction: • Poly-Sery HLB SPE cartridge (500 mg, 6 mL) • Precondition: added 5 mL of MeOH followed by 5.0 mL of Milli-Loading water sample at rate of 3.0 mL min^{-1} • Wash: added 5.0 mL Milli-Q water and cartridge was vacuum dried • Elusion: eluted with 5 mL of MeOH and vacuumed • Eluate was nitrogen blowing dried and reconstituted to 0.2 mL acetonitrile.	HPLC-MS/MS: • Agilent 1290 Series HPLC (Agilent Technologies, CA, USA). • A Zorbax SB-C18 column (100 mm × 2.1, 3.5 µm, Agilent) • Applied Biosystem SCIEX 5500 Triple Quadrupole in positive electrospray ionisation mode (ESI$^+$; Applied Biosystem, Foster City, CA, USA).	[64]
Nationwide (*n* =789)	Acetamiprid Clothianidin Dinotefuran Flonicamid Imidacloprid Imidaclothiz Thiacloprid Thiamethoxam	500 mL water samples were spiked with 125 µL of Sodium sulphite (20 gL^{-1}) and mixed isotope internal standard solution. SPE extraction: • Waters Oasis HLB cartridges (500 mg, 6 mL, Milford, MA, USA) • Precondition: added 5 mL of acetonitrile and 5 mL of water. • Loading water samples • Wash: added 5 mL of water and vacuum dried for 5 min • Elusion: eluted with 4 mL of acetonitrile and 4 mL of MeOH • Eluates were nitrogen blowing dried and reconstituted with 0.5 mL of 30% acetonitrile in water for analysis	HPLC-MS/MS • Waters ACQUITY I-Class UPLC system • Waters Acquity UPLC HSS T3 column (1.8 µm, 2.1 mm × 100 mm, Waters Corporation, Milford, MA, USA). • Waters Xevo TQS tandem mass spectrometer (Waters Corporation, Milford, MA, USA)	[65]
Nationwide (*n* = 146)	Acetamiprid Clothianidin Imidacloprid Thiacloprid Thiamethoxam	n.a.	HPLC-MS/MS • Agilent 1200 Series high-performance liquid chromatography system • Agilent G6410B triple quadrupole mass spectrometer in positive electrospray ionisation (ESI+) mode (HPLC–MS/MS, Agilent Technologies • Wilmington, DE, USA). A Zorbax SB–C18 column (100 mm × 2.1 mm, 3.5 mm; Agilent)	[66]

3. Occurrence and Distribution of Neonicotinoid Pesticides in Water

3.1. Surface Water of Taihu Lake

Taihu Lake, China's third-largest freshwater lake, is connected to the Yangtze River downstream. The land surrounding the Taihu District is characterised by complex land use, including agricultural cultivation, industrial activity, and urban development. Consequently, the lake has been significantly polluted by wastewater discharge from agricultural land, industrial plants, and residential areas, flowing through waterways and rivers within the district. Notably, Taihu Lake serves as a crucial water source for approximately six million people and numerous aquatic communities. Given its importance, water contamination has direct implications for public health and local ecological security.

Neonicotinoid pesticides (NEOs) have been extensively manufactured and used in the region. However, there is a lack of information concerning residual neonicotinoids in the surface water of Taihu Lake and the connected Yangtze River runoff. Particularly, the well-developed agriculture in the Wujin District is surrounded by arable lands, stocking areas, and fisheries. To address this knowledge gap, studies were conducted by two research teams from 2018 to 2020, focusing on the occurrence, spatial–temporal distribution, and ecological risk assessment [6,45].

In 2018, Zhou et al. conducted research to understand the spatial distribution of neonicotinoid pesticides (NEOs) in watersheds of the Wujin District [45]. They utilised Kriging interpolation modelling in conjunction with collected data. The specifics of the NEOs occurrence are recorded in Table 5. An ecotoxicological risk assessment was carried out using the risk quotient (RQ) index method. Acetamiprid, imidacloprid, and thiamethoxam were detected across all four seasons, with high detection rates of 90% for acetamiprid and 88% for imidacloprid. Notably, the maximum concentration of imidacloprid reached 36 ng L^{-1} in March, 438 ng L^{-1} in June, and 290 ng L^{-1} in autumn, surpassing the freshwater guideline value of 230 ng L^{-1} [45]. Comparing it with the other neonicotinoids, it can be inferred that imidacloprid is the most frequently used in Wujin District.

The levels of imidacloprid on the Wujin District's water surface were found to be higher than those detected in Forester Creek, California, USA, and Pearl River in the south of China. However, the study did not show significant ecotoxicological risks in the heavily polluted Wujin watershed; the RQ values for acetamiprid, imidacloprid, and thiamethoxam were all less than 0.1.

According to a subsequent study by Wang and colleagues [6], the detection frequencies for acetamiprid, clothianidin, imidacloprid, and thiamethoxam were 100%, 48%, 97%, and 83%, respectively. Among all the NEOs, imidacloprid demonstrated the highest median concentration at 31 ng L^{-1} (shown in Table 5).

Utilising an ecological risk assessment through the risk quotient (RQ) method, the study found that imidacloprid had RQ median values of 7.1, 6.1, 3.7, and 2.6 in the four seasons of the year, respectively. Furthermore, the risk index (RI) method results indicated an RI value of 6.7 for imidacloprid. These findings collectively suggest a high risk posed by imidacloprid to the aquatic community. Additionally, acetamiprid and clothianidin were identified as having a moderate to high ecological risk.

Both Zhou and Wang's studies demonstrated that the detection rate of imidacloprid was the highest among all the detected target NEOs. They also observed a similar trend where the detected concentration of IMP was higher in autumn compared to spring. Consequently, the pattern and temporal distribution of NEOs pesticide usage followed the same trend in both studies. However, the results of the RQ risk assessment in the two studies differed. Zhou's study reported that the imidacloprid in the water samples exhibited no ecotoxicity [45], whereas Wang's study reported that imidacloprid in the water samples posed a high ecological risk to the aquatic community (RQ median > 1) [6]. The potential reason for this disparity could be that Zhou's sampling areas were mainly concentrated around urban areas, while Wang's sampling area included a large agricultural zone. Since the use of neonicotinoids is typically higher in agricultural districts than in urban ones, the corresponding toxicity risk may increase with the growing use of pesticides.

Table 5. Nationwide occurrences of NEOs in the waterways of China.

Site/Location (China)	NEOs	Detection Frequency (%)	Conc Range (ng L^{-1})	Median (ng L^{-1})	Ecological Risk Assessment	References
Taihu Lake, Wujin District, Jiangsu (n = 316)	Acetamiprid Imidacloprid	90 88 31	0–38 0–236 0–53.4	8.25 65.8 10.0	Risk Quotient: No obvious risk	[45]
Taihu Lake Jiangsu (n= 208)	Acetamiprid	100	0.3–368	11	Risk Quotient and Risk index: • Imidacloprid: high • Acetamiprid: moderate-high • Clothianidin: moderate-high	[6]
	Clothianidin	48	0–391	n.d. [1]		
	Imidacloprid	97	0–907	31		
	Thiamethoxam	83	0–952	9.8		
Pearl River Guangdong (n = 66)	Acetamiprid	100	18.8–157	n.a. [2]	Probabilistic Ecological Risk Assess (chronic risk): • Acetamiprid: high • Clothianidin: high • Imidacloprid: high • Thiamethoxam: high	[25]
	Clothianidin	100	14.8–47.6			
	Imidacloprid	100	32.9–249			
	Thiamethoxam	71.4	0–52.4			
Pearl River Guangdong (n = 85)	Acetamiprid	100	3.13–67.6	9.99	Probabilistic Ecological Risk Assess (chronic risk) • 87.5% samples of Beijiang tributaries (∑NEOs > 35 ng L^{-1}) • 69% samples in Xijiang tributaries (∑NEOs > 35 ng L^{-1}) • 66.7% of samples in Dongjiang tributaries (∑NEOs > 35 ng L^{-1})	[60]
	Clothianidin	100	0.55–67.2	11.9		
	Imidacloprid	99	0.84–180	26		
	Thiacloprid	100	0.18–12.4	0.71		
	Thiamethoxam	72	4.97–102	26.7		
Pearl River, Guangzhou (n = 14)	Acetamiprid	100	6.24–77.1	34.4	Probabilistic Ecological Risk Assess (chronic risk): n.a.	[13]
	Clothianidin	100	13.1–38.0	25.2		
	Imidacloprid	100	40.1–154	78.3		
	Thiacloprid	92.9	0.44–2.97	1.03		
	Thiamethoxam	100	16.3–70.2	53.2		
Central Yangtze River From Zhijiang to Wuhan (n = 120)	Acetamiprid	100	0.26–12.0	2.50	Ecological Risk Class (Risk Quotient method): • Acetamiprid: low • Clothianidin: low • Imidacloprid: low • Nitenpyram: low • Thiacloprid: low • Thiamethoxam: low	[46]
	Clothianidin	64	n.d.-10.5	0.10		
	Imidacloprid	100	0.02–44.4	4.37		
	Nitenpyram	73	n.d.-3.50	0.34		
	Thiacloprid	87	n.d.-0.26	0.02		
	Thiamethoxam	95	n.d.-236	1.10		
Yangtze River Wuhan (n = 14)	Acetamiprid	100	3.82–9.98	4.71	n.a.	[61]
	Clothianidin	100	0.78–4.20	1.09		
	Dinotefuran	64.3	n.d.-1.20	0.29		
	Desmethyl-acetamiprid	100	0.16–0.44	0.28		
	Imidacloprid	100	3.96–28.5	7.81		
	Nitenpyram	100	0.36–8.70	0.74		
	Thiacloprid	100	0.02–0.16	0.05		
	Thiamethoxam	100	3.54–19.8	4.60		
Han River Wuhan (n = 6)	Acetamiprid	100	7.90–22.7	10.5	Compare median ∑NEOs with chronic risk threshold (35 ng L^{-1}): Long-term chronic risk to aquatic species (median ∑NEOs > 35 ng L^{-1})	[61]
	Clothianidin	100	1.10–10.5	3.43		
	Dinotefuran	83.3	n.d.-3.02	1.43		
	Desmethyl-acetamiprid	100	0.28–0.96	0.41		
	Imidacloprid	100	10.9–82.4	26.9		
	Nitenpyram	100	0.36–1.66	0.79		
	Thiacloprid	100	0.02–0.28	0.10		
	Thiamethoxam	100	5.48–64.8	18.8		
Rivers surrounding Bohai Sea (summer) (n = 72)	Acetamiprid	100	0.82–128	16.0	Ecological Risk Class (Risk quotient method): • Acetamiprid: low • Clothianidin: high • Desnitro- • Imidacloprid: low • Dinotefuran: low • Fipronil: high • Fipronil-desulfinyl: high • Fipronil-sulphide: high • Fipronil-sulfone: high • Imidacloprid- • Thiacloprid: high • Thiamethoxam: high	[62]
	Clothianidin	100	0.55–55.2	4.9		
	Desnitro-imidacloprid	100	0.42–67.3	8.6		
	Dinotefuran	47	n.d.-17.2	n.d.		
	Fipronil	94	n.d.-4.0	0.38		
	Fipronil-desulfinyl	92	n.d.-5.1	0.82		
	Fipronil-sulphide	94	n.d.-3.2	0.39		
	Fipronil-sulfone	97	n.d.-8.9	0.92		
	Imidacloprid	100	1.31–104	12.9		
	Thiacloprid	42	n.d.-5.44	n.d.		
	Thiamethoxam	100	0.54–99.8	9.2		
Bohai Sea water (summer) (n = 81)	Acetamiprid	100	0.16–0.94	0.37	Ecological Risk Class (Risk quotient): • Acetamiprid: high • Desnitro: high • Imidacloprid: n.a. • Fipronil: high • Fipronil: desulfinyl-high • Thiacloprid: high	[62]
	Desnitro-imidacloprid	88	n.d.-0.87	0.14		
	Fipronil	47	n.d.-0.13	n.d.		
	Fipronil-desulfi-nyl	12	n.d.-0.06	n.d.		
	Thiacloprid	47	n.d.-0.08	n.d.		

Table 5. *Cont.*

Site/Location (China)	NEOs	Detection Frequency (%)	Conc Range (ng L^{-1})	Median (ng L^{-1})	Ecological Risk Assessment	References
Songhua River, Harbin (n = 13)	Acetamiprid	100	0.20–10.8	0.51	SSD model: • Long-term chronic and short-term acute risk to lower trophic level aquatic species	[63]
	Clothianidin	100	1.66–13.1	2.11		
	Dinotefuran	23.1	n.d.-5.91	n.d.		
	Imidacloprid	100	10.9–83.5	11.9		
	Imidaclothiz	15.4	n.d.-0.04	n.d.		
	Thiacloprid	15.4	n.d.-1.21	n.d.		
	Thiamethoxam	100	16.3–83.5	26.7		

[1] Indicates not detected. [2] Indicates not available.

3.2. Surface Water of the Pearl River

Since the Pearl River flows through highly populated metropolitan areas, including Guangzhou, Dongguan, Shenzhen, and Hong Kong, as well as other surrounding towns, it serves as the most crucial water source for producing drinking water and supporting industrial, agricultural, and forestation activities [13,60]. Consequently, surface water contamination in the Pearl River is primarily attributed to emissions from industrial and agricultural sources. Neonicotinoid consumption in this area is increasing, with considerable amounts potentially being discharged into the soil, water, and sediments of the Pearl River due to recent forestation and crop cultivation. Imidacloprid, thiamethoxam, clothianidin, acetamiprid, and thiacloprid are five typical neonicotinoid insecticides widely applied across both rural and metropolitan areas, including Guangzhou, Dongguan, Shenzhen, and Hong Kong, all of which are situated along the important drinking water source of the Pearl River [25,60]. While only a few studies have been conducted in response to the deterioration and contamination caused by neonicotinoids in the Pearl River, three pioneering research efforts were conducted simultaneously during the period of 2018–2019, and they are summarised below.

In the study conducted by Xiong et al., the urban waterways of Guangzhou were chosen as the representative site due to their intensive agricultural and industrial activities [13,25,46]. It was reported that acetamiprid, clothianidin, and imidacloprid were detectable in all samples. The total concentration of neonicotinoid insecticides (NEOs) for each site ranged from 73.1 ± 6.9 to 375 ± 78 ng L^{-1}, with a mean of 169 ± 89 ng L^{-1} (Table 5) [25]. The primary source of NEOs is derived from practices in vegetable planting fields and sewage treatment plants. The probabilistic ecological risk assessment (ERA) approach was applied based on the construction of environmental exposure distributions (EEDs) to assess the aquatic risk of NEOs after long-term exposure. In Guangzhou, acetamiprid, clothianidin, imidacloprid, and thiamethoxam exceeded the interim chronic threshold of 35 ng L^{-1} for NEOs by 63.5%, 16.2%, 87.8%, and 17.2%, respectively [67]. It was suggested that the residues of NEOs in the urban waterways of the Pearl River posed a long-term risk to aquatic organisms.

In a study conducted by Zhang and colleagues from 2018 to 2019, water samples were collected from 49 sites across the Pearl River in Guangdong, as well as from the outlets of three wastewater treatment plants during both spring and summer [60]. Five neonicotinoid pesticides (NEOs) were detected in all 49 sampling sites along the Pearl River. The detection rates for imidacloprid, thiamethoxam, clothianidin, acetamiprid, and thiacloprid were 83–100%, 100%, 100%, 100%, and 39–91%, respectively, in the four tributaries of the Pearl River (Table 5) [60]. Among the NEOs detected in the Pearl River, imidacloprid, thiamethoxam, and acetamiprid were the three dominant species. When compared to previously reported cases of NEOs occurrences around the world, the levels of imidacloprid, thiamethoxam, and acetamiprid in the Pearl River were significantly higher than those reported in other highly contaminated areas, such as the rivers of Osaka (Japan) [40], the Guadalquivir River Basin (Spain), the Sydenham River in Canada, and various streams across the United States [60]. Concentrations of NEOs in surface water during the summer were higher than those in the spring. Due to the frequent rainfall during the summer, NEOs tended to dissolve and transfer from soil and sediment to water by soil erosion. NEOs applications in various farming lands temporally varied with the growing season of crops due to the specific characteristics of crops in different tributaries of the Pearl River.

The probabilistic ecological risk assessment (ERA) approach and ecological guidelines provide a chronic risk guideline for NEOs at 35 ng L^{-1} and an acute risk guideline at 200 ng L^{-1} [33]. Across the Pearl River system, during the spring season, 87.5% of the sampling sites in the Beijiang Tributary, 69% of sampling sites in the Xijiang Tributary, and 66.7% of sampling sites in the Dongjiang Tributary exceeded the chronic risk threshold (35 ng L^{-1}), while, in the summer, 100% of these three sampling sites exceeded the chronic risk guideline [60]. These findings suggest that there is potentially an ecological risk to the local aquatic species and invertebrates.

Guangzhou is a developed and densely populated city in China. The long-term industrialisation in urban and surrounding areas has led to the extensive use of neonicotinoid pesticides (NEOs), resulting in the severe discharge of NEOs into the soil and water. Therefore, research was conducted by Yi et al. from 2017 to 2019 [13]. In this study, high levels of NEOs were reported, with detection frequencies of approximately 100% for imidacloprid, thiamethoxam, clothianidin, and acetamiprid and a detection frequency of 92.9% for thiacloprid in surface water [13]. The total amount of five NEOs in surface water ranged from 92.6 to 321 ng L^{-1}, with a geometric mean of 174 ng L^{-1}. Imidacloprid accounted for 35% of the total NEOs detected, ranging from 40 to 154 ng L^{-1}. In most cases, the detected levels of NEOs were comparable to or even beyond the levels detected in previous studies in Japan and Canada [13].

A correlation analysis was conducted to understand the impact of the water quality on the distribution and occurrence of neonicotinoid pesticides (NEOs) in surface water [13]. Water quality parameters such as temperature, pH, dissolved oxygen, and redox potential were correlated with the levels of NEOs in the water. Temperature had a significant effect on the total NEOs levels, although this effect was not consistent for each individual NEO. It was observed that the degradation half-life (DT_{50}) for imidacloprid and thiamethoxam decreased with an increase in the pH, indicating the two NEOs are more degradable and mobile under alkaline conditions compared to neutral and acidic conditions [13]. Clothianidin, on the other hand, showed minimal sensitivity to changes in the pH. Additionally, higher dissolved oxygen (DO) levels were found to stimulate the transformation of NEOs in water. A significantly positive correlation between the nitrogen and phosphate levels and NEOs indicates that nitrogen and phosphate are common sources of NEOs in the Guangzhou section of the Pearl River [13].

Furthermore, it was observed that the western and front river routes of the Guangzhou section of the Pearl River experienced more severe neonicotinoid contamination, approximately two times higher in surface water, compared to the rear river route. Based on the results of the probabilistic ecological risk assessment (ERA), it was suggested that the NEOs levels at all 14 sampling sites along the Pearl River exceeded the threshold for long-term risk, and 42.9% of the sampling sites exceeded the threshold for short-term acute risk [13].

3.3. Surface Water of the Yangtze River

The Yangtze River, which is the longest river in China and serves as the vital national water source, flows across the southern region of the nation. Information regarding NEOs contamination and the resulting human health and ecological risks in the central part of the Yangtze River has been limited. Therefore, Mahai and colleagues conducted an investigation into NEOs contamination in the Central Yangtze River, spanning from Zhijang to Wuhan [57].

The investigation revealed that acetamiprid, imidacloprid, and thiamethoxam were the dominant NEOs in the water samples (refer to Table 5). The detection frequency of acetamiprid (100%), imidacloprid (100%), and thiamethoxam (95%) in the water samples was the highest, followed by THCP (87%), NTP (73%), and clothianidin (64%) [57]. Additionally, the median concentration of these six NEOs followed this order: imidacloprid

(4.37 ng L^{-1}) > acetamiprid (2.5 ng L^{-1}) > thiamethoxam (1.10 ng L^{-1}) > NTP (0.34 ng L^{-1}) > clothianidin (0.1 ng L^{-1}) > THCP (0.02 ng L^{-1}) [57]. It was suggested that this situation could be attributed to the mainstream manufacturing and consumption of acetamiprid, imidacloprid, and thiamethoxam up to the year 2015 [57]. DM-acetamiprid, the metabolite of acetamiprid, was detected in 88% of the water samples, and the concentration of DM-acetamiprid (0.22 ng L^{-1}) was ten times lower than that of acetamiprid. The detected levels of NEOs in the Central Yangtze River were higher than those found in various other countries and regions, such as the Chieng Khoi Watershed in Vietnam, the Guadalquivir River in Spain, Sydney in Australia, and seven stream basins in Iowa, USA. Notably, the levels of acetamiprid in this study [57] were higher than those reported in most other countries, including Japan, the USA, and Portugal.

As shown in Table 5, there are variations in the concentrations of individual NEOs, with higher levels detected in the summer compared to spring, consistent with the results obtained from the Pearl River in China [57]. This could be attributed to the increased mobility of NEOs in surface water runoff and soil during the high precipitation of summer [63].

The risk quotient (RQ) method was employed to assess the potential ecological risks of the detected NEOs, and the RQs of all six NEOs were found to be lower than 0.1, indicating a low risk to the aquatic system.

In addition, Wan and colleagues (2019) investigated the occurrence of NEOs in the Yangtze River and Han River [61]. There are seasonal variations in the occurrence of NEOs in raw water sources; the total NEOs, imidacloprid, clothianidin, dinotefuran, and thiacloprid showed higher concentrations in July compared to May [61]. Moreover, greater levels of NEOs were observed in the Han River than in the Yangtze River. The median level of NEOs in the Han River exceeds the ecological threshold (for long-term exposure) of 35 ng L^{-1}, indicating an ecological risk to aquatic species [61]. The high contamination of NEOs in the Han and Yangtze Rivers is primarily caused by the extensive usage of NEOs in the areas surrounding the rivers, the high transport of NEOs from agricultural lands, and deficiencies in their removal at drinking water treatment plants [61]. Due to the prolonged persistence of NEOs, the consumption of drinking water is recognised as the most direct pathway for human exposure to NEOs [61,62]. The demand for monitoring NEOs in drinking water sources is increasing as potential health concerns arise. Recent studies have reported the presence of NEOs in drinking water worldwide. However, investigations into NEOs in drinking water sources in China and their consumption remain relatively limited. This includes assessing occurrences across China and different exposure routes (oral intake, inhalation, and dermal absorption/percutaneous penetration). Only a few studies have been completed in recent years.

3.4. Surface Water of the Bohai Sea

Many previous studies have investigated neonicotinoid pesticides (NEOs) in the water and sediments of natural freshwater systems, but information about NEOs occurring in seawater is scarce. The Bohai Sea area comprises Liaodong Bay, Bohai Bay, and Laizhou Bay, surrounded by Liaoning Province, Hebei Province, Shandong Province, and the Tianjin municipality. As a result of industrialisation and agricultural activities, there has been a significant increase in water pollution in coastal and river systems, primarily due to the large populations residing in these areas. Specifically, NEOs are considered persistent compounds in water and sediments, which can be discharged into the coastal area, but there is limited knowledge about the ecological risk assessment of NEOs in seawater systems. To address this gap, Naumann and co-workers launched a project to monitor the occurrence of NEOs and conduct ecological risk assessments in the Bohai Sea and the surrounding river systems [62].

Generally, the rivers and tributaries surrounding Bohai and Laizhou Bays were the most contaminated areas, while the rivers flowing into the Bohai Strait and North Yellow Sea exhibited relatively low levels of NEOs. The detected levels of NEOs in Bohai were higher in the summer than in autumn, primarily due to the greater quantity of neonicotinoids applied in the fields during spring and summer. In Laizhou Bay, the detected levels of NEOs in the summer were higher than those detected in the winter, mainly attributed to point sources from the manufacturing of neonicotinoid pesticides around the cities of Laizhou Bay [62].

Regarding individual NEOs, it was observed that acetamiprid, clothianidin, imidacloprid, and thiamethoxam were significantly higher in the summer than in the winter, reflecting that these NEOs are predominantly used pesticides in agricultural activities surrounding the coastal area of the Bohai Sea. Acetamiprid was the most abundant individual NEO, with a detection frequency reaching as high as 100% in both summer and autumn [62]. Acetamiprid was the only NEO detected in all rivers and seawater samples from the summer and fall in 2018. The high detection frequency indicates the intense usage of NEOs in the study area and the persistence of acetamiprid in natural water bodies.

For the classic, well-established NEOs, clothianidin and imidacloprid were frequently detected in the rivers but rarely in the seawater samples. For the novel NEOs, fipronil and fipronil-sulfone detection were negligible in seawater compared to their frequent detection in river water [62]. A reasonable explanation could be the dilution and degradation of NEOs, along with adsorption into the riverbeds. The study suggested that the degradation of the NEOs was potentially influenced by water temperature and the proportion of transmitted sunlight [62].

A fingerprint analysis was conducted using the approach adopted by the USEPA. The results showed a high homogeneity of contamination sourced from agricultural activities with the application of numerous well-established NEOs. Only the NEOs manufacturing industries around Laizhou Bay were identified as particular point sources during autumn and winter. Therefore, it was concluded that riverine discharges are the main source of contamination in the Bohai Sea, and diffuse sources are the primary contributors to river contamination [62].

The ecological risk to aquatic species was assessed using the risk quotients (RQs) method based on the European technical guidance document on risk assessment (EC 2003) [62]. The ecological risk assessment was estimated to be medium to high, based on the results of the RQs assessment. Fipronil and its transformation products were classified as having a medium to high potential risk, primarily based on freshwater standards and criteria [62]. It is required to carry out further investigations of the impact of NEOs on marine organisms.

3.5. Surface Water of the Songhua River

Previous studies on water contamination in the Songhua River primarily focused on heavy metals, polycyclic aromatic hydrocarbons, polychlorinated biphenyls, antibiotics, and other pollutants. However, the contamination of neonicotinoid pesticides (NEOs) in the Songhua River remains unknown [63]. To address this knowledge gap, Liu and colleagues conducted a comprehensive investigation of NEOs occurrence in the Harbin section of the Songhua River, including the mainstream and four tributaries [63]. They detected seven NEOs species in the surface water, with concentrations ranging from 30.8 to 135 ng L^{-1}. Notably, the detection frequencies of imidacloprid, thiamethoxam, clothianidin, and acetamiprid in the surface water were very high, reaching 100%. Imidacloprid and thiamethoxam were the dominant NEOs species, with median concentrations of 41.4 ng L^{-1} and 62.3 ng L^{-1}, respectively (Table 5) [63]. The combined concentrations of imidacloprid and thiamethoxam accounted for over 80% of the total NEOs in the different samples. In comparison, the NEOs concentrations in the Harbin section of the Songhua River were much higher than those reported in the Yangtze River and the Guangzhou section of the Pearl River [63]. Furthermore, the NEOs concentrations in the mainstream surface water were higher than those detected in the surface waters of the tributaries, suggesting that pollutants from the tributaries were the source of NEOs contamination in the mainstream surface water. To assess the aquatic ecological risk, the species sensitivity distribution (SSD) model was applied. The concentration of imidacloprid-equivalent residue (IMIeq) in the mainstream was lower than the acute hazardous concentration for 5% of the species values (HC5), while, in most of the tributaries, it exceeded the chronic HC5. The risk potency factor (RPF) method was used to estimate human exposure by comparing the calculated estimated daily intake (EDI) values with the threshold reference dose (RfD) value [63]. Among all the age groups, thiamethoxam had the highest intake, indicating the greatest risk compared to the other NEOs. Infants had the highest EDI, followed by toddlers, children, teenagers, and adults. The high intake of NEOs in infants could be attributed to their higher food and fluid consumption per unit of body weight compared to the other age groups. It is worth noting that the estimated maximum total IMIeq EDI (31.9 ng/kg in infants) was three orders of magnitude lower than the threshold provided by the USEPA (57,000 ng kg^{-1} bw.d^{-1}) [63]. However, the intake via nondietary ingestion, inhalation, and dermal contact was underestimated, potentially affecting the data on human exposure to NEOs [63].

3.6. Drinking Water of the Cities of Wuhan and Hangzhou

Wan and colleagues (2019) investigated the occurrence of NEOs in the drinking water of Wuhan (Table 6) [61]. Despite the conventional treatment process involving aeration, coagulation, flocculation, sedimentation, sand filtration, and chlorination, there was a deficiency in removing NEOs from finished drinking water. The median concentration of acetamiprid was reduced from 5.14 ng L^{-1} to 3.08 ng L^{-1}, and the median concentration of thiacloprid was reduced from 0.05 ng L^{-1} to 0.04 ng L^{-1} [61]. Only 40% of acetamiprid and 20% of thiacloprid were removed, with negligible removal of the remaining NEOs. In most cases, the observed NEOs levels in drinking water were comparable to those detected in the USA and Canada [61]. There was seasonal variations in the median NEOs concentrations, with the highest median NEOs levels (96.2 ng L^{-1}) observed in July, followed by those in May (30 ng L^{-1}), October (10.2 ng L^{-1}), and January (4.41 ng L^{-1}), which attributed to the most intensive application of insecticides and the highest water flow during that month [61].

An exposure assessment was conducted using the estimated daily intake (EDI) method, which calculated the imidacloprid-equivalent residue (IMIeq) and daily water ingestion rate (WIR) for different age groups. The results were then compared to the lowest reference dose (RfD) for the final evaluation. Infants were identified as the most susceptible group compared to the other age groups, with the NEOs intake by infants being approximately four times higher than that of adults [61].

The maximum EDI of the total NEOs or IMIeq through drinking tap water was lower than the reference dose (RfD) by two or three orders of magnitude. However, the increasing trend of NEOs in drinking water continues to raise concerns on many fronts [61].

Furthermore, Lu and colleagues conducted a study on the occurrence of neonicotinoid insecticides (NEOs) in Hangzhou City, Zhejiang Province. In household tap water, acetamiprid and IMI were the most frequently detected NEOs in the tap water samples, with detection frequencies of 83% and 82%, respectively [59]. It was observed that the NEOs levels decreased from the source water through the water treatment plant to household tap water. Unlike the results observed in a previous study [68], the current drinking water treatment processes were found to remove over 50% of NEOs.

The risk potency factor (RPF) method was applied for exposure and risk assessment, and a Monte Carlo simulation was used to calculate the chronic daily intake (CDI) of total NEOs. The maximum CDIs were 10.2 and 12.4 ng kg^{-1} in the present study, with the CDIs for children being higher than those for adults. However, the maximum CDI was three orders of magnitude lower than the acceptable daily intake (ADI) or reference dose (RfD) for imidacloprid, indicating a low health risk. When compared to the daily intake from consuming fruits and vegetables in a previous study [59], it was concluded that exposure to NEOs through the consumption of fruits and vegetables is higher than through the drinking water route.

Table 6. Nationwide occurrence of NEOs in the drinking water samples of China.

Site/location (China)	NEOs	Detection Frequency (%)	Conc Range (ng L^{-1})	Median (ng L^{-1})	Ecological Risk Assessment	References
Wuhan (n = 165)	Acetamiprid	n.d. [1]	0.65–20.7	2.78	Estimation of human exposure to NEOs through ingestion (L kg^{-1} bw^{-1} day^{-1}) of water (RPF method): • Infants: 0.090 • Toddlers: 0.031 • Children: 0.029 • Teenagers: 0.016 • Adults: 0.020	[61]
	Clothianidin		n.d.-8.98	1.28		
	Dinotefuran		n.d.-54.8	0.2		
	Desmethyl-acetamiprid		0.05–0.80	0.2		
	Imidacloprid		1.16–76.7	4.3		
	Nitenpyram		n.d.-54.8	0.2		
	Thiacloprid		n.d.-0.26	0.04		
	Thiamethoxam		0.38–47.0	3.54		
Hangzhou (n = 71)	Acetamiprid	n.d.	0–16.6	6.15	Total IMI$_{RPF}$ (ng L^{-1}) in tap water (Risk assessment of total neonics intake through drinking water consumption) • Mean: 17.19 • Median: 11.4 • Range: 0–105.4	[59]
	Clothianidin		2.9–7.5	3.85		
	Dinotefuran		3.4–25	7.75		
	Imidacloprid		1.5–10.6	4.5		
	Nitenpyram		1.9–22.6	6.05		
Nationwide (n = 84)	Acetamiprid	94	0.002–69.2	2.72	In China, the average EDI (median, age from 2 -> 65, ng kg^{-1} bw^{-1} day^{-1}) of NEOs via tap water consumption. (Estimated daily taken method): • acetamiprid: 0.032 • clothianidin: 0.030 • dinotefuran: 0.025 • imidacloprid: 0.042 • thiacloprid: 0.002 • thiamethoxam: 0.024	[64]
	Clothianidin	92	0.005–104	5.46		
	Dinotefuran	90	<0.03–312	4.55		
	Imidacloprid	99	<0.02–68.3	7.59		
	Thiacloprid	86	0.002–74.2	0.38		
	Thiamethoxam	87	<0.03–214	4.5		
Nationwide (n = 789)	Acetamiprid	94	8.10–182	0.42	n.a. [2]	[65]
	Clothianidin	70	13.4–98.8	0.16		
	Dinotefuran	26	3.02–13.7	n.d.		
	Flonicamid	4.4	n.d.-0.70	n.d.		
	Imidacloprid	84	24.8–233	0.86		
	Imidaclothiz	4.9	n.d.-0.62	n.d.		
	Thiacloprid	42	0.20–7.18	n.d.		
	Thiamethoxam	68	29.1–232	0.28		
Nationwide (n= 146)	Acetamiprid	78.1	n.d.-15.5	0.47	n.a.	[66]
	Clothianidin	80.1	n.d.-109	0.73		
	Imidacloprid	83.6	n.d.-55	1.76		
	Thiacloprid	24	n.d.-3.11	0.04		
	Thiamethoxam	63	n.d.-88.5	1.2		

[1] Indicates not detected. [2] Indicates not available.

3.7. Drinking Water of China Nationwide

He and co-workers also conducted a study to investigate the occurrence of neonicotinoid pesticides (NEOs) in drinking water in China (Table 6) [64]. The study found that NEOs were ubiquitous in the tap water collected from 38 cities. Among them, six targeted NEOs were detected with high detection frequencies from 86% (thiacloprid) to 99% (imidacloprid) [64]. Based on the median of the detected NEOs concentrations, the concentrations of NEOs followed the trend of imidacloprid (7.59 ng L^{-1}) > clothianidin (5.46 ng L^{-1}) > dinotefuran (4.55 ng L^{-1}) > thiamethoxam (4.50 ng L^{-1}) > acetamiprid (2.72 ng L^{-1}) > thiacloprid (0.38 ng L^{-1}). The total concentration of the six NEOs was 25.4 ng L^{-1} [64].

Higher concentrations of NEOs were found in Eastern, Southern, and Southwestern China compared to those observed in Northern and Northwestern China. This difference could be attributed to pesticide usage patterns in China, with the results indicating an increasing trend from north to south across the country.

The NEOs exposure risk was assessed using the risk quotient (RQ) approach. Age groups were categorised based on the Fourth China Total Diet Study, including 2–7 year olds, 8–12 year olds, 13–19 year olds, 20–50 year olds, 51–65 year olds, and those over 60 years old [64].

It was observed that the estimated daily intake (EDI) of individual NEOs decreased with increasing age. Among all the age groups, the EDI of imidacloprid was the highest, followed by the EDIs of clothianidin, thiamethoxam, and dinotefuran [64].

Furthermore, Mahai and colleagues conducted a nationwide investigation into the occurrence of NEOs in tap water (Table 6) [65]. Among all the tap water and groundwater samples, acetamiprid had the highest detection frequency at 93%, followed by imidacloprid (82%), clothianidin (69%), and thiamethoxam (66%) [65]. In all the tap water samples, the dominant NEOs were acetamiprid, imidacloprid, clothianidin, thiamethoxam, DM-acetamiprid, imidacloprid-urea, and DN-imidacloprid, all with detection frequencies greater than 60% [65].

It was observed that clothianidin was positively correlated with thiamethoxam ($p < 0.001$), consistent with the results obtained from previous studies [65]. This correlation is primarily attributed to the generation of clothianidin from the transformation of thiamethoxam in water. The highest concentrations of NEOs were found in surface-derived tap water, followed by groundwater and deep groundwater-derived tap water. The pattern of NEOs contamination was as follows: South China (ΣNEOs = 27.6 ng L^{-1}) > Central China (ΣNEOs = 8.07 ng L^{-1}) > East China (ΣNEOs = 7.39 ng L^{-1}) > Southwest China (ΣNEOs = 3.28 ng L^{-1}) > Northeast China (ΣNEOs = 1.16 ng L^{-1}) > Northwest China (ΣNEOs = 0.20 ng L^{-1}) [65]. Clothianidin, imidacloprid, and thiamethoxam were the predominant NEOs in South China, Central China, and Southwest China, while acetamiprid, imidacloprid, and thiamethoxam were the major NEOs in East China and Northeast China [65]. Acetamiprid and imidacloprid were the most significant NEOs in Northwest China and North China. The NEOs registered in China are primarily used for rice and wheat, with relatively smaller amounts used in other crops [65]. Therefore, provinces that predominantly plant rice and wheat tend to have higher NEOs contents in their drinking water, while regions mainly planting corn and other crops tend to have lower NEOs contents. The risk quotient (RQ) method was applied to assess the cumulative human exposure to the total NEOs [65].

In addition, Zhang and colleagues conducted a similar study on the occurrence of neonicotinoid pesticides (NEOs) in drinking water (Table 6) [66]. The most frequently detected NEO was imidacloprid, with a detection frequency of 83.6%, followed by clothianidin (80.1%) and acetamiprid (78.1%) [66]. Except for thiacloprid (24.0%), the detection frequencies of the other NEOs were higher than 60%. The geometric mean (GM) concentrations of the NEOs detected in all the water samples followed this descending order: imidacloprid (1.76 ng L^{-1}) > thiamethoxam (1.20 ng L^{-1}) > clothianidin (0.73 ng L^{-1}) > acetamiprid (0.47 ng L^{-1}) > thiacloprid (0.01 ng L^{-1}) [66].

Spatially, with the exception of Northcentral (84.6%) and Northwest (88.9%) China, where the detection frequencies of the NEOs were slightly lower, in the other four regions, the detection frequencies of the NEOs were all 100% [66]. The concentrations of the sums of the five NEOs in tap water from different regions followed this order: southcentral (45.5 ng L^{-1}) > east-central (14.9 ng L^{-1}) > southwest (8.41 ng L^{-1}) > northeast (3.61 ng L^{-1}) > northcentral (3.28 ng L^{-1}) > northwest (1.10 ng L^{-1}) [66]. This suggests that the NEOs levels in China's tap water tend to decrease from the southeast to the northwest.

The relative potency factor (RPF) approach was used for assessing the exposure risk of NEOs. The seasonal influence on NEOs exposure via percutaneous exposure (NPE) in children of all ages followed this order: summer > spring = autumn > winter [66]. Regarding NEOs exposure through drinking water from different sources, the general order was tap water > direct drinking water = well water > bottled water. This highlights the need for improvements in the removal of NEOs during water treatment by further technical upgrades.

4. Conclusions and Further Works

Conclusions and recommendation of future works can be drawn from this review and are detailed as below:

(1) Neonicotinoids (NEOs) have been extensively used in agriculture, horticulture, and household applications. However, neonicotinoids pose threats to human health and ecological security, leading to substantial health and environmental concerns associated with these substances.
(2) China currently lacks water quality criteria for NEOs, though some developed countries like the Netherlands, Germany, the USA, and Canada have established water quality guidelines or water quality criteria for NEOs.
(3) It is crucial to establish analytical methodologies for NEOs with both the parent compounds and derivative metabolites/by-products. The solid-phase extraction method is commonly used for sample pretreatment, and high-performance liquid chromatography coupled with mass spectrometry is the prevalent technique to simultaneously detect multiple neonicotinoids and their metabolites.
(4) NEOs have been detected in rivers, lakes, seas, and treated drinking water sources across China. Their ubiquitous presence over the past decades can be attributed to their widespread use in agriculture and horticulture, resulting in detected levels ranging from 1 to 100 ng L^{-1}. Acetamiprid, clothianidin, imidacloprid, thiacloprid, and thiamethoxam were the most frequently detected NEOs. Contamination primarily originated from surface water runoff near agricultural areas, sewage, and wastewater effluent.
(5) Most monitoring studies have concentrated on the southern and southeast regions of China, particularly the Taihu Lake District, Yangtze River Delta, and Pearl River Delta, while information from Northern China remains relatively limited. This review stresses the need for more comprehensive investigations to bridge the knowledge gap, especially in remote and developing regions. Additionally, given the high levels of residual NEOs in Southern China, future research should expand to specific sites surrounding problematic areas in the region.
(6) Overall, a moderate to high long-term ecological risk was associated with NEOs in most of the reported studies, with acute ecological risks seldom reported. Although many of the studies indicated low to moderate NEOs occurrence, there has been an increasing trend in human health risks in recent years.
(7) As the production and consumption of NEOs continue to rise in China, there is an urgent need for the monitoring and management of NEOs and their metabolites in water and other environmental media to mitigate the potential health risks.
(8) Given the limited number of studies on NEOs characteristics and contamination across China, this study underscores the urgent necessity for nationwide research on this subject.

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