Research on Pesticide Residue Monitoring Technologies and Prospects for Monitoring System Construction: Postprint

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Date: 2017-10-21T00:00:00+00:00

Abstract

The issue of pesticide chemical contaminant residues has become one of the major food safety concerns of international significance. In China, pesticide detection in commercially available agricultural products remains prevalent, with residues of banned and highly toxic pesticides continuing to threaten the security of the public's "vegetable basket."As a critical point for source supervision of agricultural product quality, pesticide residue monitoring technology has evolved from classical chromatography and mass spectrometry to high-resolution mass spectrometry, achieving intelligent and automated innovations in qualitative screening of non-targeted pesticide analytes. Based on investigation and analysis of over 4,000 SCI papers on pesticide residue detection from 1990-2016 and the developmental status of pesticide residue monitoring systems both domestically and internationally, this article—integrating achievements of the author' s team over the past decade in research, development, and practical application of high-resolution mass spectrometry-internet-data science/geographic information system (GIS) ternary fusion technology—focuses on discussing core technical approaches required to enhance source supervision and risk traceability of agricultural product quality. It proposes recommendations for planning and implementing a national major science and technology special project to construct a large-scale pesticide residue database for commercially available edible agricultural products in China, aiming to provide technical support for implementing the "Pesticide Use Zero Growth Action"and "Advancing Healthy China Construction" initiatives outlined in the national "13th Five-Year Plan" outline, thereby promoting forward-shifted food safety supervision and safeguarding public food safety.

Full Text

Special Topic: Science & Technology Promoting Agricultural Supply-side Structural Reform

Prospect for Research on Pesticide Residue Monitoring Techniques and Construction of Monitoring Systems

Chinese Academy of Inspection and Quarantine

Pesticide chemical contaminant residues have become one of the major food safety concerns worldwide. Pesticides are still frequently detected in agricultural products sold in China, and residues of banned, highly toxic pesticides continue to threaten the safety of the public' s "vegetable basket."

Abstract

Pesticide chemical contaminant residues have become one of the major food safety concerns worldwide. Pesticides are still frequently detected in agricultural products sold in China, and residues of banned, highly toxic pesticides continue to threaten the safety of the public' s "vegetable basket." As a key control point for source regulation of agricultural product quality, pesticide residue monitoring techniques have evolved from conventional chromatography and mass spectrometry to high-resolution mass spectrometry, achieving intelligent and automated innovation in qualitative screening of non-target pesticides. Based on investigation and analysis of over 4,000 SCI papers on pesticide residue detection from 1990–2016 and the current development status of pesticide residue monitoring systems at home and abroad, this article combines the results of tri-element fusion technology development and practical application of high-resolution mass spectrometry-internet-data science/geographical information system (GIS) achieved by the authors' team over the past decade. It focuses on the core technical means needed to improve source monitoring and risk traceability of agricultural product quality, and proposes planning and implementation recommendations for national major scientific and technological projects to construct a big database of pesticide residues in commercially available agricultural products in China. This aims to provide technical support for implementing the national "13th Five-Year Plan" initiatives of "Zero Growth Action for Pesticide Use" and "Promoting Healthy China Construction," to advance food safety monitoring forward, and to ensure public food safety.

Keywords: pesticide residue, food safety, high-resolution mass spectrometry, data science, geographical information system (GIS)

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Pesticides are a "double-edged sword" that play a crucial role in protecting crop growth, increasing agricultural yields, and ensuring storage quality. However, due to their biological activity, residual pesticides inevitably impact food safety and the ecological environment. Countries worldwide have implemented monitoring and surveillance systems for pesticides and chemical contaminants from farm to table. The European Union, United States, and Japan have established relatively complete legal frameworks and regulatory agencies, setting maximum residue limits (MRLs) for pesticides in agricultural products. While strictly controlling pesticide use, these countries continuously strengthen and emphasize the monitoring of harmful residues and the development of detection technologies, forming highly sophisticated monitoring systems.

As a major agricultural country, China is among the world' s largest producers and consumers of pesticides. From 2000–2015, China' s chemical pesticide technical material production increased from 600,000 to 3.74 million tons annually. Pesticide chemical contaminants represent a primary source of food safety contamination. Although various Chinese authorities have different residue monitoring plans, they have not formed a strict legal framework or a unified national monitoring system. The limited residue data resources from various departments play only a minor role in food safety regulation. China has not yet established a big data resource for pesticide residues in agricultural products, yet such fundamental data is crucial for food regulation. Fortunately, China' s detection technology in this field has now reached world-advanced levels, providing full capability to catch up quickly in these fundamental research areas.

Current Status of Pesticide Residue Monitoring Systems

International Status

The strategic importance of pesticide and chemical contaminant monitoring has long been established worldwide. As early as 1976, WHO, FAO, and UNEP jointly established the Global Environment Monitoring System/Food Contamination Monitoring and Assessment Programme to understand food contamination status in member countries, assess food contaminant intake, protect human health, and promote trade development. Maximum residue limits (MRLs) are food safety standards, international trade thresholds, and important criteria for food safety monitoring systems. The EU, US, and Japan have established 162,248, 39,147, and 51,600 MRL standards respectively, while China's national standard "GB 2763-2016—Maximum Residue Limits of Pesticides in Food" implemented in June 2017 only specifies 4,140 MRLs for 433 pesticides, representing a significant gap with EU and Japanese standards and posing major challenges for developing pesticide residue analysis technologies and MRL standards.

The US has established three major pesticide residue monitoring systems since the 1970s: the National Residue Program (NRP), Pesticide Residue Monitoring Program (PPRM), and Pesticide Data Program (PDP), monitoring over 500 pesticide varieties and building a pesticide chemical contaminant residue database. In 1996, the EU launched the Community Programme for Pesticide Residue Monitoring, including both EU-level and member state systems, monitoring 839 pesticide varieties. Japan's Positive List System monitors 542 pesticides, ensuring scientific pesticide application, reducing residue levels, promoting green development, and improving food safety. These databases play significant roles in food safety regulation.

Domestic Status

China has not yet established a long-term mechanism for pesticide residue monitoring systems, and the situation regarding pesticide and chemical contaminant residues remains severe. No strict systematic legal framework guarantees the monitoring system. Although authorities such as the Ministry of Agriculture, China Food and Drug Administration, and General Administration of Quality Supervision have implemented monitoring programs with some achievements, their limited role in overall food safety monitoring has prevented effective pesticide and veterinary drug residue monitoring. Research from our team's national science and technology support project "Research and Demonstration of High-Throughput Detection Technology for Pesticide Chemical Contaminants in Food" reveals that residual pesticide risks in China's "vegetable basket" remain severe, with highly toxic and banned pesticides still being detected. Pesticide residue data challenges the effective implementation of proven regulations like GMP, GAP, and HACCP. Fruit and vegetable pesticide residues cannot be ignored and require prevention-focused, forward-positioned regulation. Establishing a comprehensive pesticide residue monitoring system to ensure farm-to-table food safety is urgently needed.

Development Trends in Pesticide Residue Monitoring Technology

As an important technical support means for monitoring systems, the scientific validity and operability of detection methods are the cornerstone for ensuring effective system operation. Analysis of 4,678 SCI papers on pesticide residue detection in agricultural products from 15 journals revealed 214 detection technologies, with the most frequently used being LC-MS/MS, GC-MS, LC-UV, and GC-ECD. Chromatography (with selective detectors) was used in 1,432 papers, and mass spectrometry in 2,091 papers, making these the two most widely applied technologies in residue analysis [Figure 1: see original paper].

Mass Spectrometry Becomes Mainstream Technology

Since Thomson developed the first mass spectrometer in 1912, over 100 years have passed. Early mass spectrometers were mainly used for isotope determination and inorganic element analysis. Beginning in the 1940s, they were applied to organic analysis, and the 1960s saw the emergence of GC-MS, greatly expanding mass spectrometry applications and making it an important instrument for organic analysis. Computer applications accelerated mass spectrometry development. After the 1980s, new technologies emerged including FAB, ESI, APCI, LC-MS, ICP-MS, and FTMS. These new ionization techniques and mass spectrometers have enabled significant progress, with mass spectrometry now widely applied in chemistry, materials, environment, geology, energy, pharmaceuticals, forensics, life sciences, food science, and medicine. In agricultural product pesticide residue detection, mass spectrometry has developed rapidly.

GC-MS technology has developed steadily since 1992. Due to advances in ESI and APCI, LC-MS/MS has been leading since 2003. High-resolution mass spectrometry (HRMS) such as TOF/MS and Orbitrap had no application in residue analysis before 2002, but applications have increased significantly since then. HRMS' s unique accurate mass identification capability makes it the future direction for residue analysis [Figure 2: see original paper].

High-Resolution Mass Spectrometry Becomes the Direction for Non-Target Screening

Unlike low-resolution mass spectrometry, HRMS provides high mass resolution (>10,000 FWHM), high mass accuracy (<5 ppm), and high scan rates. Common HRMS instruments include FTICR, Orbitrap, TOF/MS, and Q-TOF/MS. The main principle distinguishes target compounds based on different flight times of ions with different mass-to-charge ratios in the flight tube. After ionization, target compounds enter the flight tube where a pulsed electric field applies identical electric potential energy converted to ion kinetic energy, making ion flight time proportional to the square of their mass-to-charge ratio, enabling mass-to-charge ratio determination. TOF/MS can also be tandem with quadrupoles for ion filtration, selection, and collision-induced fragmentation to obtain fragment ion information.

Due to HRMS's capability to simultaneously screen numerous target compounds without quantity limitations in full-scan mode, multi-residue screening applications mainly use two approaches: (1) qualitative determination based on accurate mass, chromatographic retention time, and isotope distribution; (2) using in-source fragment ions as auxiliary qualitative evidence. To date, Q-TOF/MS and other HRMS applications in complex matrix pesticide residue analysis remain preliminary, with limited research reports on establishing pesticide mass spectral libraries and non-target screening of over 1,000 pesticides without standards.

R&D of High-Resolution Pesticide Residue Monitoring Technology

Developing Electronic Standards to Replace Physical Standards

Using GC-Q-TOF/MS or LC-Q-TOF/MS, we developed primary accurate mass databases and secondary fragment ion spectral libraries for over 1,200 commonly used pesticides worldwide. Based on this, we established a unique electronic ID (electronic identification standard) for each pesticide, replacing traditional identification methods that use physical pesticide standards as references. This achieves a leapfrog development from targeted detection to non-targeted screening of pesticide residues, realizing high speed (30 minutes), high throughput (over 1,000 pesticides), high precision (0.0001 m/z), high reliability (over 10 identification points), and high informatization, automation, and electronicization. This completely solves the drawbacks of targeted detection technology, with analysis speed and method efficiency unimaginable for traditional methods. The detection capability is internationally leading, far exceeding current US, EU, and Japanese pesticide residue detection capabilities, greatly improving agricultural product quality and safety assurance. The covered fruit and vegetable categories reach 18 types with over 150 varieties, with 85% belonging to species listed in the national MRL standard (GB 2763-2016), closely reflecting market realities. This saves resources, reduces pollution, and fully achieves green development, environmental friendliness, and clean efficiency.

Developing HRMS-Internet-Data Science Tri-Fusion Technology for Automated Report Generation

Given the highly digital, informational, and electronic nature of non-target pesticide residue detection technology, massive analytical data challenges traditional statistical analysis methods, urgently requiring new big data collection, transmission, statistical analysis, and intelligent analysis systems. Addressing difficult problems in pesticide residue detection data analysis—high data dimensionality, complex relationships, and high analysis requirements—we solved key technologies for associated storage and querying of "multi-national MRL standards-agricultural product classification-properties of over 1,000 pesticides." We proposed multi-dimensional cross-analysis methods for pesticide residue detection data and comprehensive evaluation and early warning models for pesticide residue contamination. We established four foundational databases including multi-national MRL standards, enabling associated access and retrieval of pesticide residue baseline data to provide standard bases for detection result determination.

We independently developed a pesticide residue data acquisition system and constructed a pesticide residue detection results database. Our "data acquisition-information supplement-derivative merging-banned pesticide processing-contamination level determination" data fusion and processing model enables rapid online collection and fusion of multi-residue detection data, precise determination against multi-national MRLs, and dynamic addition and real-time updating of the detection results database, providing scientific data support for national food safety decision-making.

We independently developed an intelligent analysis system for massive pesticide residue data, proposing multi-dimensional cross-analysis methods and comprehensive evaluation and early warning models. This achieves automatic statistics of 18 pesticide residue indicators and automatic generation of 5 reports from multi-dimensional perspectives including agricultural products, pesticides, regions, and multi-national MRLs, plus automatic generation of comprehensive evaluation and early warning information based on statistical results, 最终实现 "one-click download." A fully illustrated pesticide residue detection report can be automatically generated within 30 minutes, greatly improving accuracy and efficiency—unmatched by traditional analysis methods—providing an effective tool for pesticide residue data analysis.

Developing HRMS-GIS Tri-Fusion Technology for Visualized Risk Traceability

Associating pesticide residue data with geographic data enables new applications of China maps driven by pesticide residue data. Core technologies include: (1) multi-spatial resolution, multi-scale (national-provincial-prefectural) expression of crop pesticide residue characteristics; (2) statistical analysis and mapping of various pesticide residue characteristics by agricultural product type; (3) reflecting spatial and crop-type distribution characteristics and quantitative indicators of various pesticide residues; (4) displaying residue violations by region and product type according to Chinese, EU, and Japanese MRL standards. Using HRMS+Internet+GIS multi-technology fusion, we designed visualization systems for target pesticides, food names, and origins with multi-dimensional spatial characteristics, creating two products: the "Atlas of Pesticide Residue Levels in Commercial Fruits and Vegetables from 31 Provincial Capitals/Municipalities" and the "Online Mapping System for Pesticide Residues in Commercial Fruits and Vegetables from 31 Provincial Capitals/Municipalities," achieving visualized management of pesticide residue detection, traceability, and early warning on a "smart one-map" platform. This provides scientific data support for industry self-discipline, government regulation, and third-party supervision based on spatial visualization.

Application of High-Resolution Pesticide Residue Monitoring Technology

The two HRMS technologies (GC-Q-TOF/MS and LC-Q-TOF/MS) have different advantages for analyzing multi-pesticide residues in complex matrices and can complement each other during detection, offering high throughput and universal applicability. Combined, they have screened over 1,000 pesticide residues in 22,328 commercial fruit and vegetable samples from 638 sampling points across 284 districts/counties in 31 provincial capitals/municipalities, completing detection reports for each location. This has preliminarily clarified the pesticide residue status in commercial fruits and vegetables in China, including 20 regular characteristics such as main distribution areas, varieties, toxicity, residue levels, and differences among various agricultural products .

The two HRMS technologies apply to 18 categories and 146 types of fruits and vegetables, covering over 85% of China' s fruit and vegetable catalog. They provide powerful pesticide residue discovery capability. By replacing physical standards with electronic standards for qualitative identification, they achieve a leap from targeted to non-targeted detection, enabling automation and electronicization of pesticide residue detection. Applied to analysis of 146 fruit and vegetable varieties from 31 provincial capitals/municipalities, they provide accurate mass spectrometry data. The two methods complement and verify each other, demonstrating that their combination is an effective analytical strategy for comprehensive rapid screening and multi-residue monitoring. In summary, this new technology has clarified the existence status and regular characteristics of pesticide residues in 18 categories and 146 types of fruits and vegetables in China, establishing the "baseline" of pesticide residues in commercial fruits and vegetables from 31 provincial capitals/municipalities. This provides important scientific data support for implementing the "13th Five-Year Plan" initiatives to "strengthen governance of pesticide and veterinary drug residue exceedances," "implement zero-growth action for chemical fertilizer and pesticide use," and "improve inspection frequency and coverage with full-chain traceability management."

Measures and Recommendations

Create a "National Monitoring Engineering Research Center for Pesticide Residues in Commercial Agricultural Products"

We should closely track international non-targeted pesticide residue detection technology development to continuously improve detection capabilities. We should further develop the HRMS+Internet+Data Science tri-fusion technology into upgraded pesticide residue big data intelligent analysis software, and the HRMS+Internet+GIS tri-fusion technology into the "Online Mapping System for Pesticide Residues in Commercial Agricultural Products" for visualization. We should build and organize over 30 alliance laboratories for pesticide residue monitoring to create a pesticide chemical contaminant monitoring technology platform. This platform would conduct year-round cyclic detection of pesticide residues, heavy metals, and biotoxins in commercial agricultural products (fruits, vegetables, tea, and grains) nationwide; perform risk assessment for key regions, key products, and key pesticides; and provide effective technical support and scientific data for national management departments' decision-making and supervision. We should conduct research on food safety and nutrition, major cutting-edge topics, and strengthen international cooperation and exchange to identify research topics for international tracking, parallel running, and leading.

Create a "China Pesticide Residue Database for Commercial Agricultural Products"

We should establish a three-tier (national-provincial-prefectural) China pesticide residue database for commercial agricultural products, expanding capacity from the demonstration project' s 31 provincial capitals/municipalities and 284 districts/counties to cover 31 provinces/autonomous regions/municipalities with over 2,000 districts/counties. Sampling points should expand from over 600 to 3,000–5,000, covering over 85% of the population (up from 25%). The database should include pesticide residue data for over 150 commercial agricultural products from 31 provincial capitals/municipalities and over 400 prefectural-level administrative regions with permanent populations exceeding 500,000, with plans to expand to harmful metal elements and biotoxins. All database sources should come from 30 alliance laboratories following "six unifications"standardized operations (unified sampling standards, unified sample preparation, unified detection methods, unified data upload format, unified statistical analysis model, unified participation in international/EU proficiency testing and blind sample testing) in a closed-loop operation to ensure data uniformity, integrity, security, reliability, and scientific validity.

We plan annual sampling and screening for all prefectural-level cities and quarterly sampling for all municipalities and provincial capitals, with an estimated annual sample volume of 100,000 cases. Using the three-tier architecture, we can track pesticide residue dynamics in real-time across 31 provincial capitals/municipalities and over 400 prefectural administrative regions. Compared with the previous demonstration project, the database capacity will expand 15–20 fold, establishing China' s first "Pesticide Residue Database for Commercial Agricultural Products." We should provide national-provincial-prefectural pesticide residue detection reports and recommend their inclusion in procurement plans for national, provincial, and municipal food safety departments as important regulatory tools, including annual national reports, annual provincial reports, annual prefectural reports, and quarterly reports for municipalities and provincial capitals. We should expand development of the "Online Mapping System Software" and atlases, recommending their inclusion in government procurement plans as important regulatory tools.

The informatization of pesticide residue monitoring technology, intelligent processing of big monitoring data, and visualization of pesticide residue risk traceability will play important roles in improving China' s pesticide residue monitoring system and significantly transforming food safety conditions. Conducting surveys on agricultural product pesticide chemical contaminant residue levels to understand the baseline, planning and establishing real-time dynamic detection databases, and incorporating the "31 Provincial Capitals/Municipalities Pesticide Residue Detection Reports" into national government procurement plans will encourage various government departments to utilize the massive data resources from pesticide residue detection reports, atlases, and online mapping systems, transforming them into advanced productive forces to truly implement national "13th Five-Year Plan" actions. This work is not only a food safety issue but also relates to national stability, image, and long-term peace.

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TABLE:1 Pesticicide Residue Monitoring Technology Research and Monitoring System Construction Prospect

Regular Characteristics Discovered from Big Data Statistical Analysis of Pesticide Residues

1. Compared with developed countries (EU, US, Japan), China' s pesticide MRL standards face challenges of low levels and insufficient quantity
2. Only a small portion of massive survey data applies China' s standards; missing standards put China at a disadvantage
3. Top fruit/vegetable varieties with most detected pesticide types
4. Top fruit/vegetable varieties with highest average detection frequency
5. Types and frequencies of detected highly toxic, extremely toxic, and banned pesticides
6. Pesticide residue detection rates in provincial capitals/municipalities—pesticide residues are widespread
7. Pesticide types detected in various fruits/vegetables, with combined detection by two technologies
8. Pass rates of pesticide residues in commercial fruits/vegetables—basic safety level ensured

9. Characteristics of pesticide residue detection levels (compared using Chinese, EU, and Japanese standards)
10. Characteristics of pesticide varieties detected in single samples (non-detected, 1-3 types, 4-6 types, 7 types)
11. Characteristics of pesticide varieties detected in similar samples (non-detected, 1-3 types, 4-6 types, 7 types)
12. Toxicity characteristics of detected pesticides (slightly toxic, low toxicity, moderately toxic, highly toxic, extremely toxic, and banned pesticides—types and proportions)
13. Detected pesticide varieties and frequencies (sorted by region, agricultural product, etc.)
14. Safety assessment of detected pesticides (non-detected, detected but not exceeded, exceeded) sorted by Chinese, EU, and Japanese standards
15. Top fruit/vegetable varieties with highly toxic, extremely toxic, and banned pesticide detections
16. Top fruit/vegetable varieties with highest frequencies of highly toxic, extremely toxic, and banned pesticides
17. Characteristics and differences of widespread pesticide residues in commercial fruits/vegetables
18. Characteristics and differences of pesticide residues at sampling points
19. Characteristics and differences of pesticide use in provincial capitals/municipalities

Note: Figure translations are in progress. See original paper for figures.

Source: ChinaXiv —Machine translation. Verify with original.