PESTICIDE RESIDUE RESEARCH GROUP

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Evaluation of Orbitrap UPLC-HRMS to the analysis of pesticides in various commodities

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INTRODUCTION

High resolution mass spectrometry is a technique which helps to overcome some typical limitations of triple quadrupole mass spectrometers. High resolution instruments provide accurate mass measurement. Spectrometers working in full scan mode can register unlimited number of compounds. This feature allows to perform non-target analysis and retrospective analysis. Moreover HRMS saves time because optimisation of acquisition parameters for each compound is not required. Hybrid instruments are also equipped in quadrupole mass filter and collision cell. Thanks to this it is possible to perform MS/MS experiments.

Orbitrap is a high resolution mass analyser. This analyser is build from two curved electrodes: central electrode (which is sustained at high voltage) and outer electrode (which surrounds central electrode). Ions are injected into the Orbitrap in small packets. Strong electrical field inside the trap pushes them towards the equator thus initiating axial oscillations, while rotation around the central electrode keeps ions from falling onto the central electrode. Axial oscillations are detected and after that time-domain signal is converted into a frequency and then into m/z spectrum by Fourier transform.

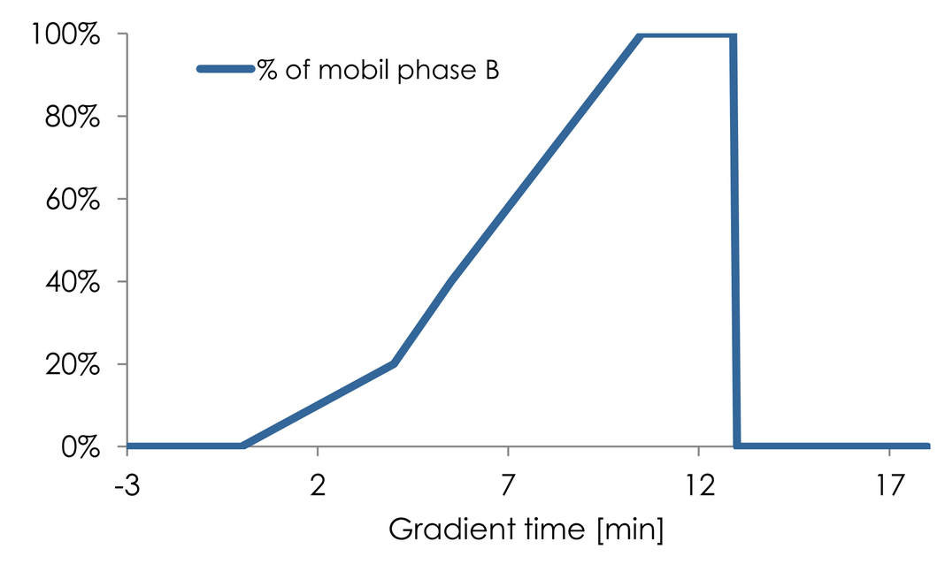
EXPERIMENTAL

Analysed matrices:
- tomato
- pepper
- orange
- green tea

Extraction method: Citrate QuEChERS
Number of spiked pesticides:163
Final sample dilution: 5 times (0.2 g/mL)

Mobil phase:
- A: 98% H_2O 2% MeOH 5mM $HCOONH_4$ 0.1% HCOOH
- B: 98% MeOH 2% H_2O 5mM $HCOONH_4$ 0.1% HCOOH

Flow: 0.4 mL/min
Gradient time: 15 min
Column: Thermo Accucore C18
150 mm x 2.1mm x 2.6μm



Acquisition mode: full scan
Resolutions (FWHM at m/z 200):
-17500
-35000
-70000
AGC target: 1e6
Maximum IT: 200 ms
Scan range: 100 – 800 m/z
Mass calibration: external

RESULTS

Target list

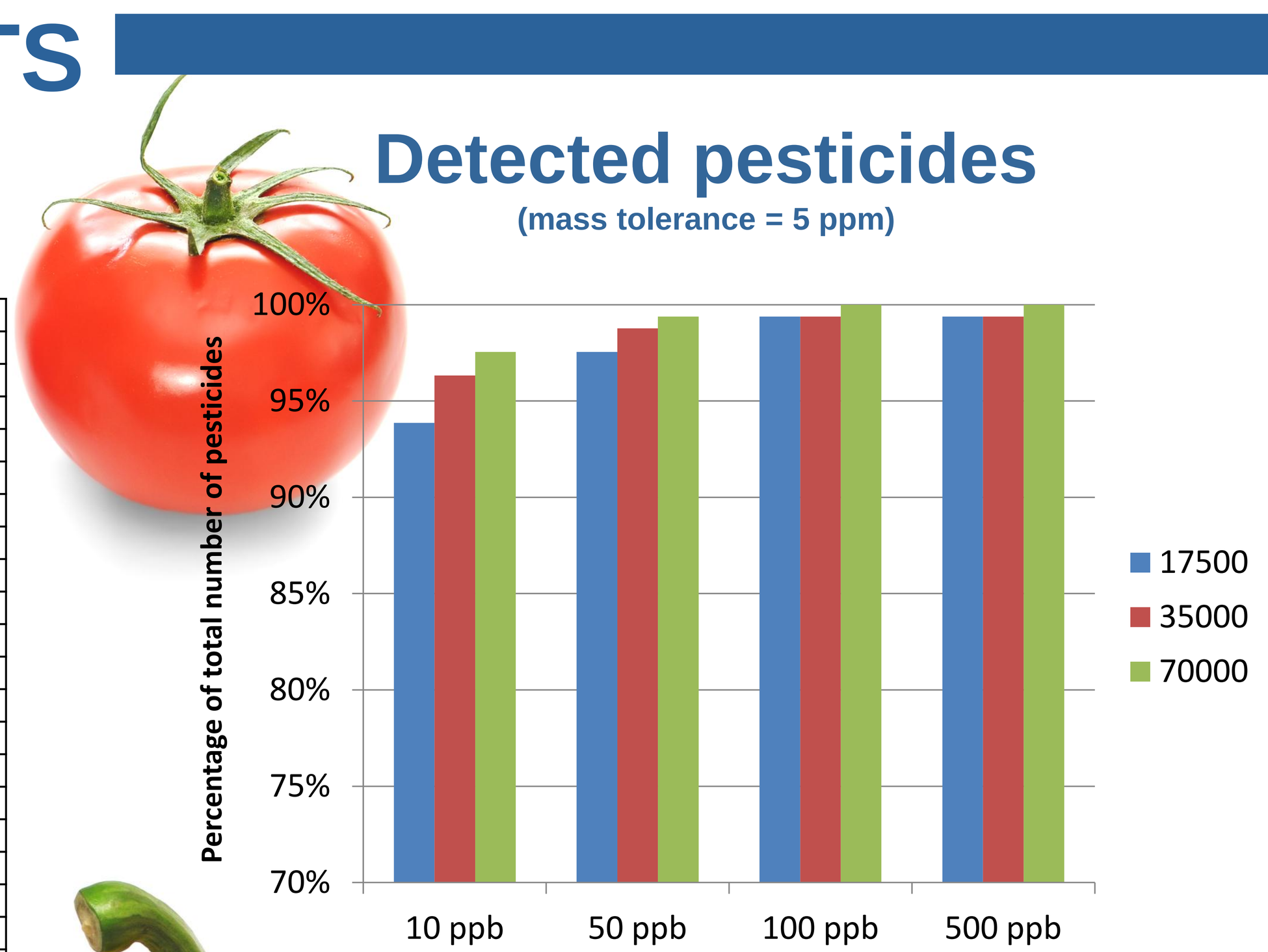
2,4-D	Metalaxyl-M
3-hidroxycarbofuran	Metconazole
Acephate	Methamidophos
Acetamiprid	Methidathion
Aldicarb	Methiocarb
Aldicarb Sulfone	Methiocarb Sulfone
Aldicarb Sulfoxide	Methiocarb Sulfoxide
Azinphos-methyl	Methomyl
Azoxystrobin	Methomyl
Benomyl	Methoxyfenozide
Bitertanol	Metobromuron
Boscalid	Monocrotophos
Bromuconazole	Myclobutanil
Bupirimate	Nitenpyram
Buprofezin	Omethoate
Carbaryl	Oxadixyl
Carbendazim	Oxydemeton-methyl
Carbofuran	Paclobutrazol
Chlorantraniliprole	Paraoxon Methyl
Chlorfenvinphos	Penconazole
Chlorpyrifos	Pencycuron
Chlorpyrifos-methyl	Pendimethalin
Clofentezine	Phenthoate
Clothianidin	Phosalone
Cymoxanil	Phosmet
Cyproconazole	Phosmet Oxon
Cyprodinil	Phoxim
Cyromazine	Pirimicarb
Demeton-S-methylsulfone	Pirimiphos-methyl
Desmethyl Pirimicarb	Prochloraz
Diazinon	Profenofos
Dichlorvos-d6	Propamocarb
Dicrotophos	Propiconazole
Diethofencarb	Propoxur
Difenoconazole	Propyzamide
Diflubenzuron	Prothioconazole
Dimethoate	Prothioconazole-desthio
Dimethomorph	Pymetrozine
Diniconazole	Pyraclostrobin
Dithianon	Pyrethrin
Dodine	Pyridaben
Epoxiconazole	Pyrimethanil
Ethion	Pyriproxyfen
Ethirimol	Quinoxyfen
Ethoprophos	Rotenone
Fenamidone	Spinosad
Fenamiphos	Spirodiclofen
Fenamiphos Sulfone	Spiromesifen
Fenamiphos Sulfoxide	Spiroxamine
Fenarimol	Tebuconazole
Fenazaquin	Tebufenozide
Fenbuconazole	Tebufenpyrad
Fenhexamid	Teflubenzuron
Fenitrothion	Terbuthylazine
Fenoxycarb	Tetraconazole
Fenpropathrin	Thiabendazole
Fenpropimorph	Thiacloprid
Fenpyroximate	Thiamethoxam
Fenthion	Thiodicarb
Fenthion Oxon	Thiophanate-methyl
Fenthion Oxon Sulfone	Tolclofos-methyl
Fenthion Oxon Sulfoxide	TPP
Fenthion Sulfone	Triadimefon
Fenthion Sulfoxide	Triadimenol
Fipronil	Triazophos
Flonicamid	Trichlorfon
Fluazifop	Trifloxystrobin
Flubendiamide	Triflumuron
Fludioxonil	Triticonazole
Flufenoxuron	Zoxami
Fluopyram	
Fluquinconazole	
Flusilazole	
Flutriafol	
Formetanate	
Fosthiazate	
Haloxyfop	
Hexaconazole	
Hexythiazox	
Imazalil	
Imidacloprid	
Indoxacarb	
Iprovalicarb	
Isofenphos-methyl	
Isoprocarb	
Kresoxim-methyl	
Linuron	
Lufenuron	
Malaoxon	
Malathion	
Malathion-d10	
Mandipropamid	

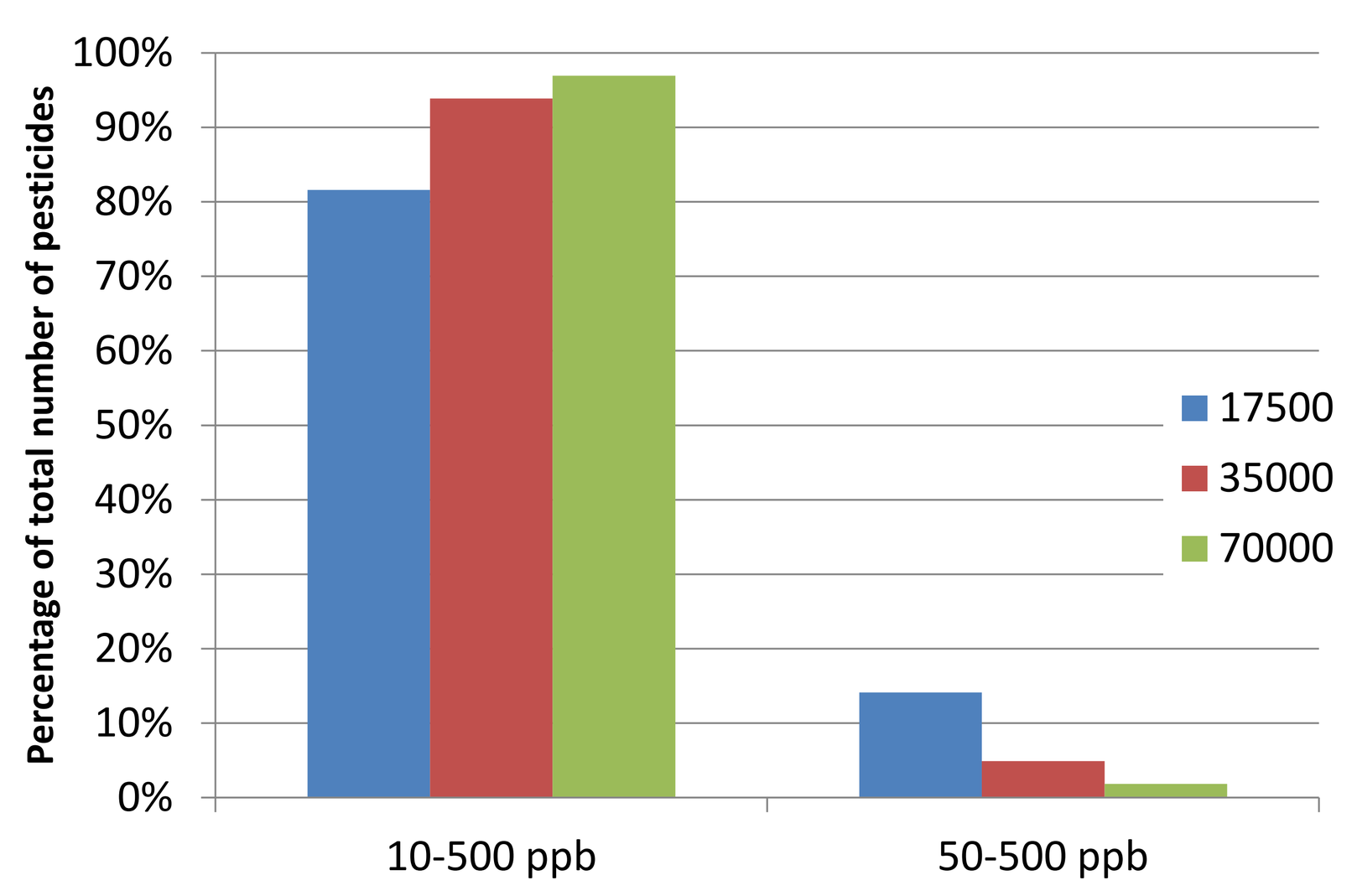
Detected pesticides
(mass tolerance = 5 ppm)

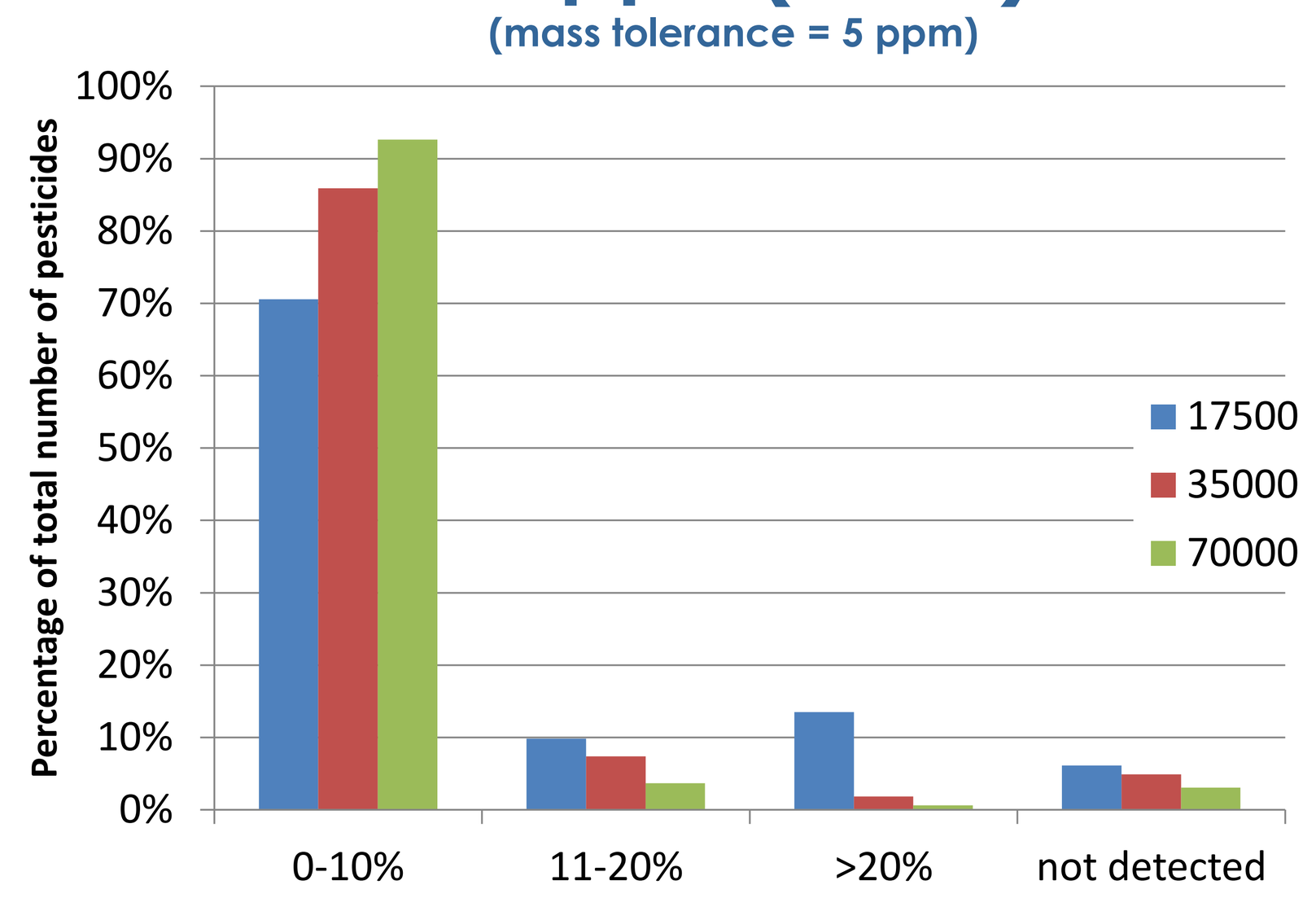
Linearity
(mass tolerance = 5 ppm)

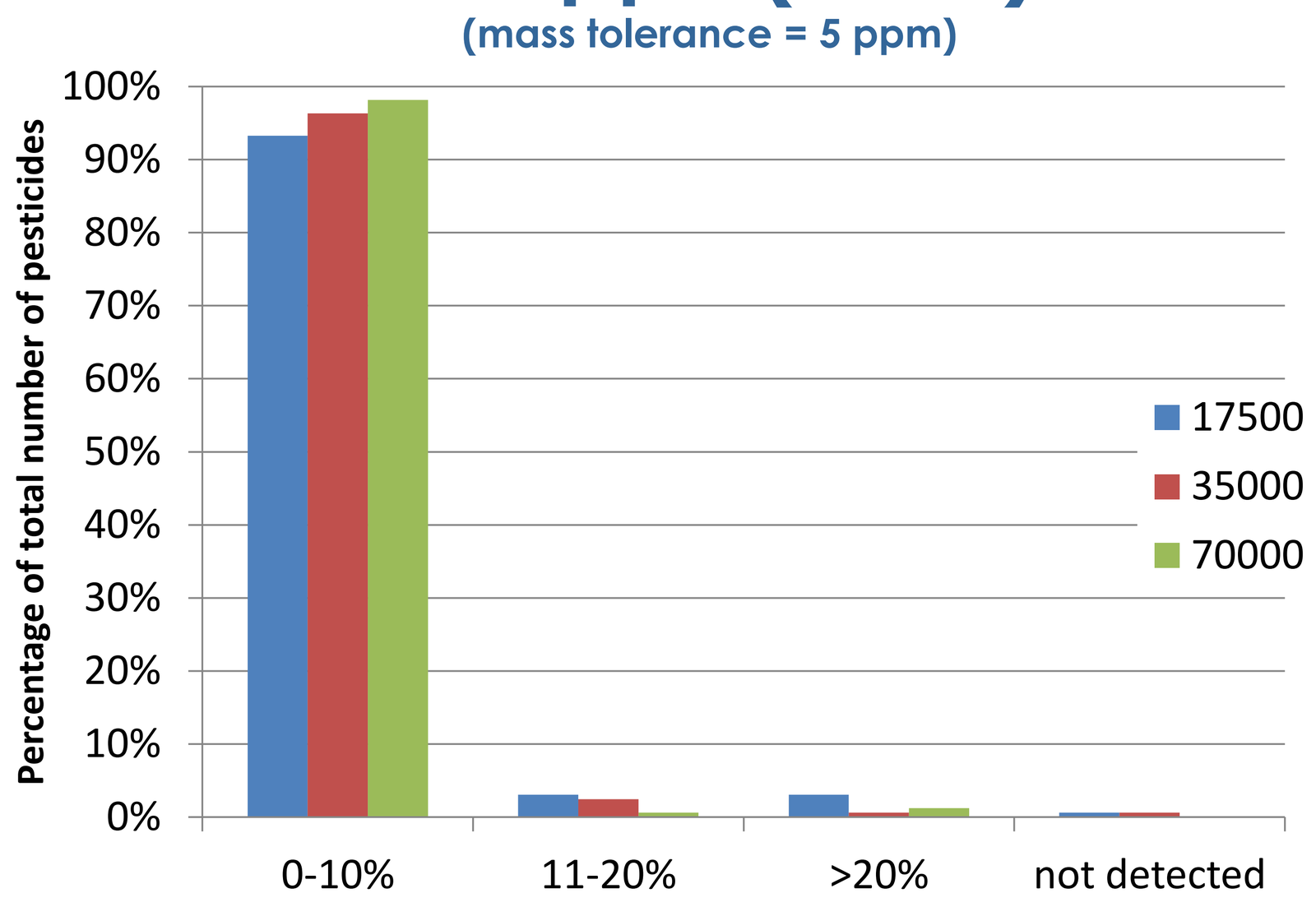
Relative standard deviation 10 ppb (n = 3)
(mass tolerance = 5 ppm)

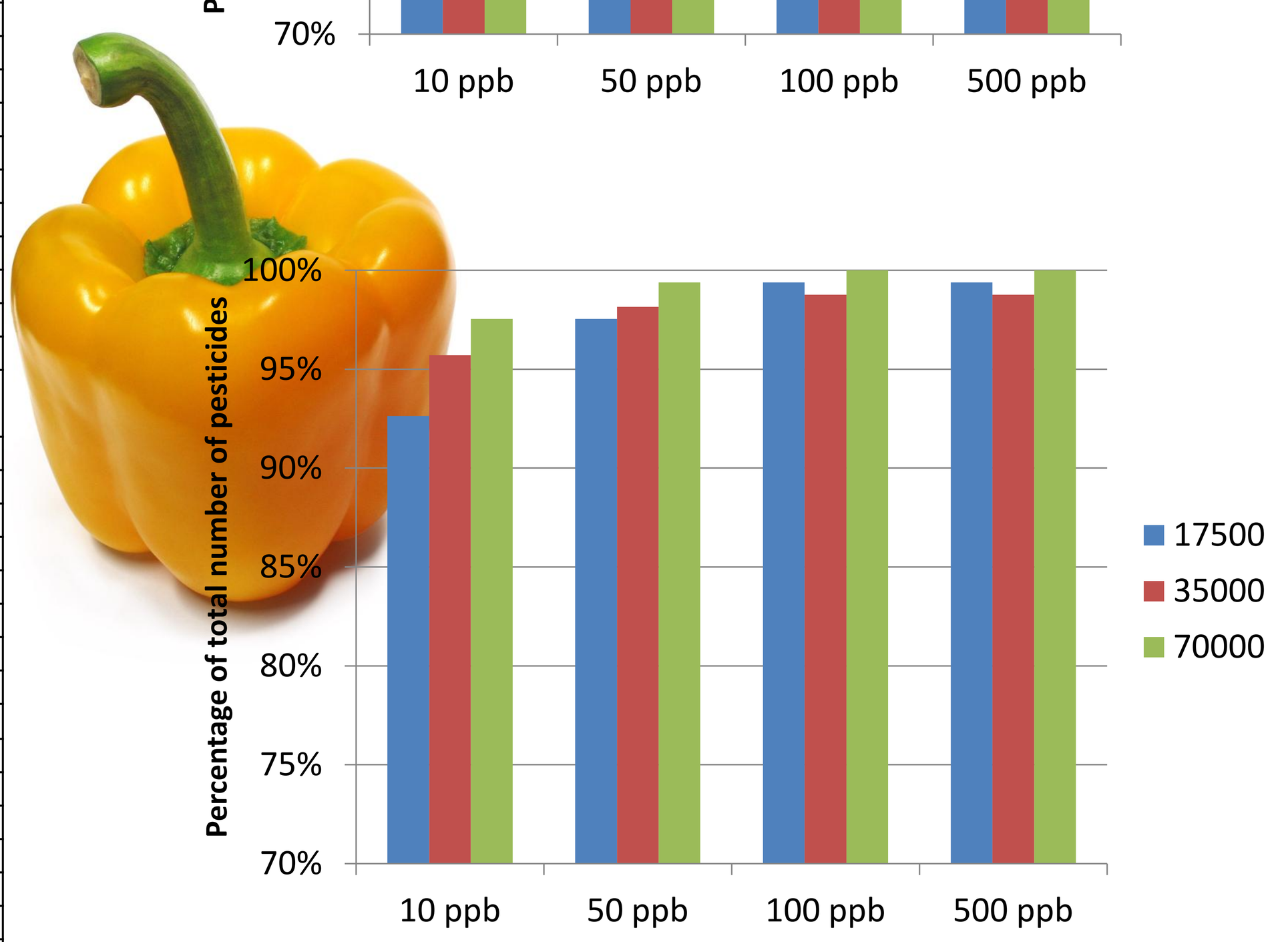
Relative standard deviation 100 ppb (n = 3)
(mass tolerance = 5 ppm)

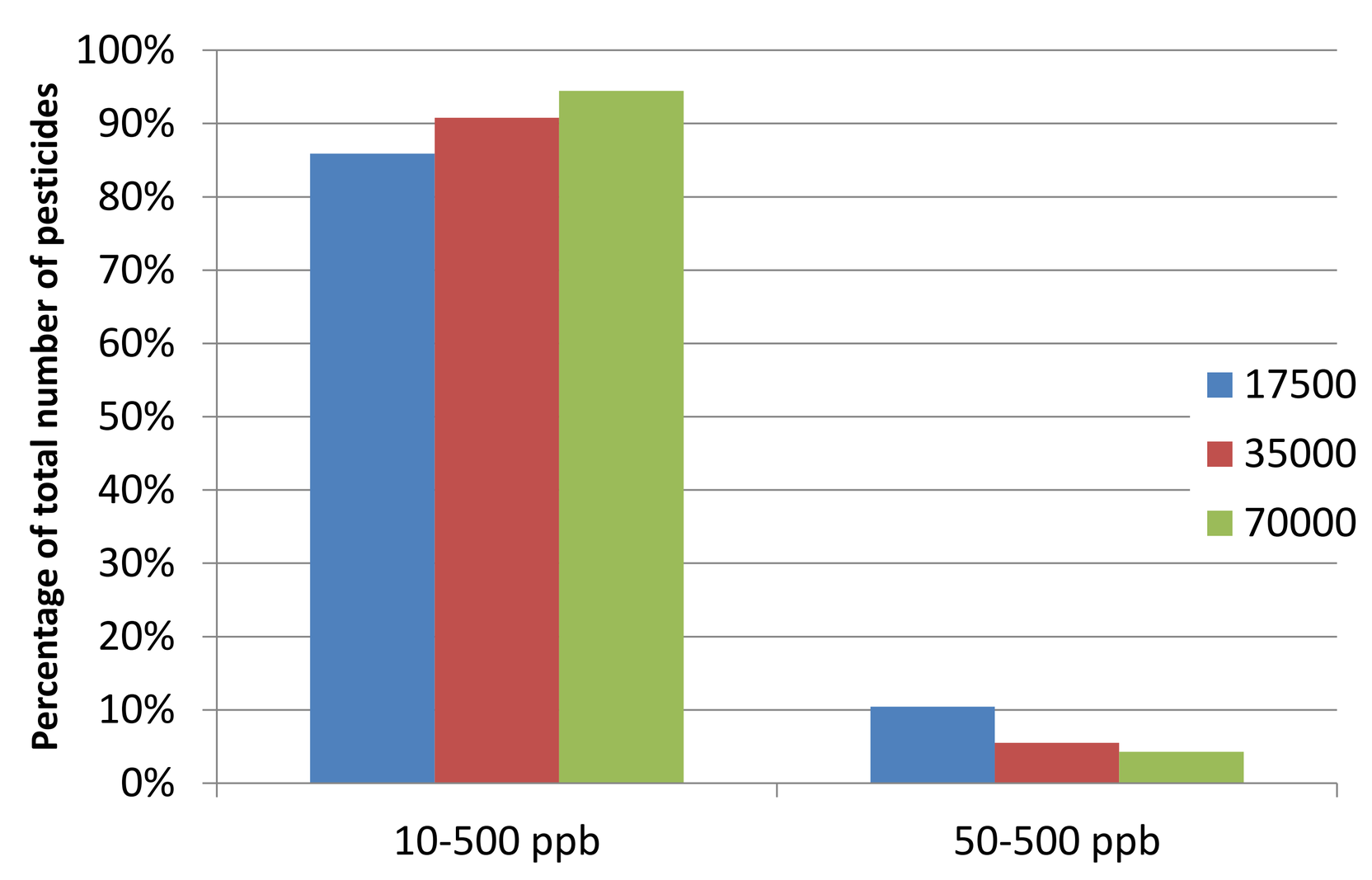


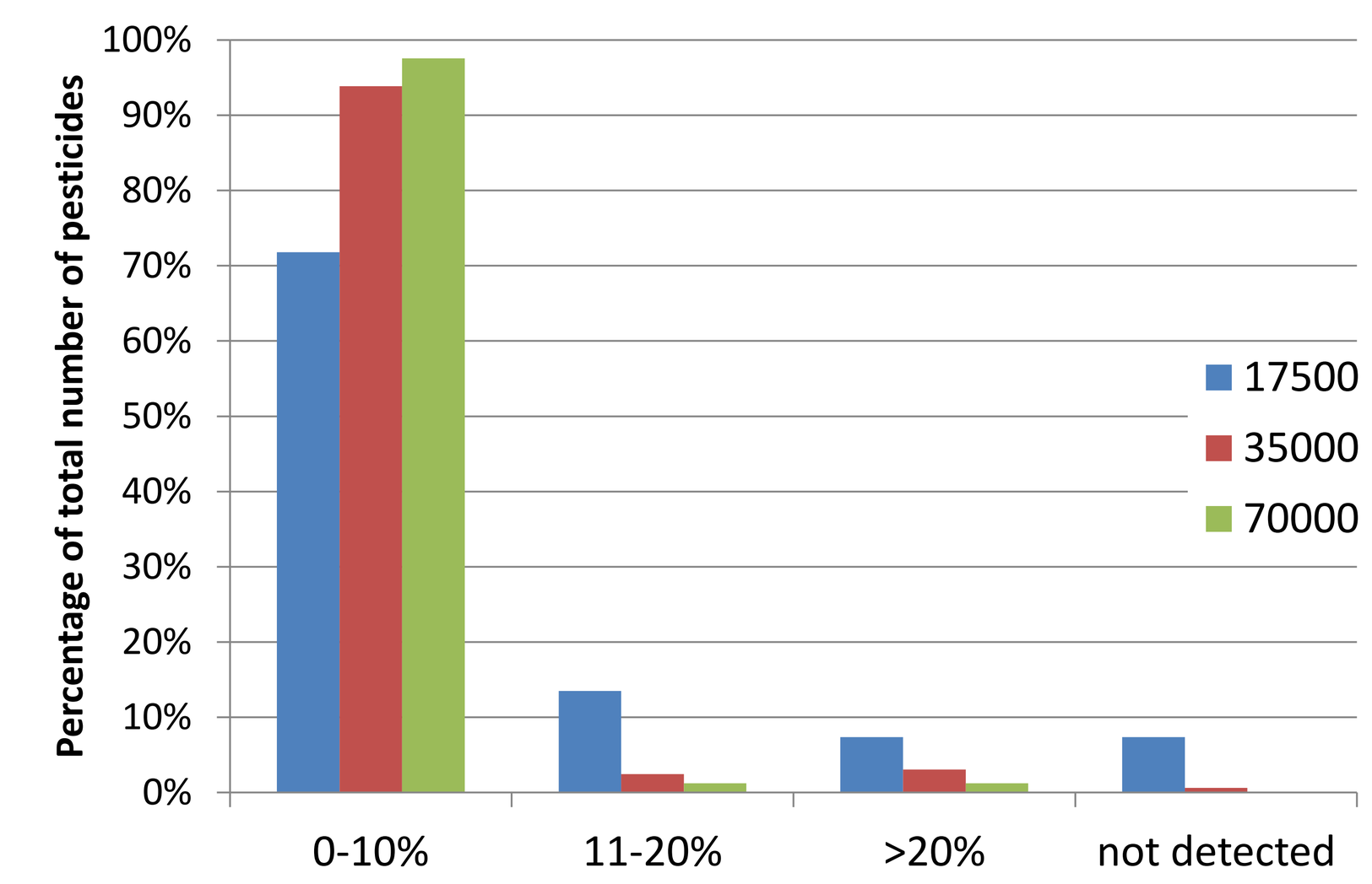


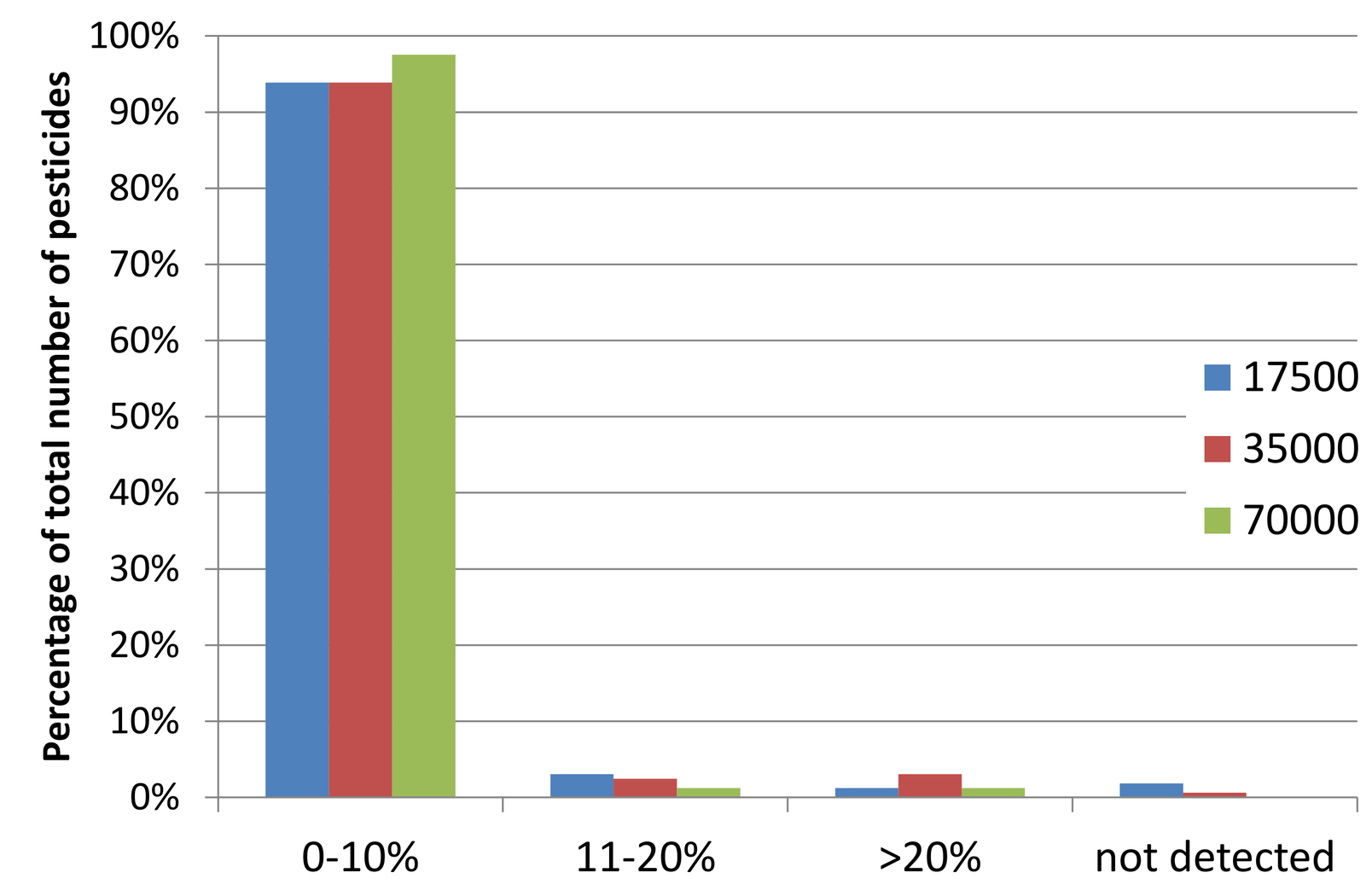


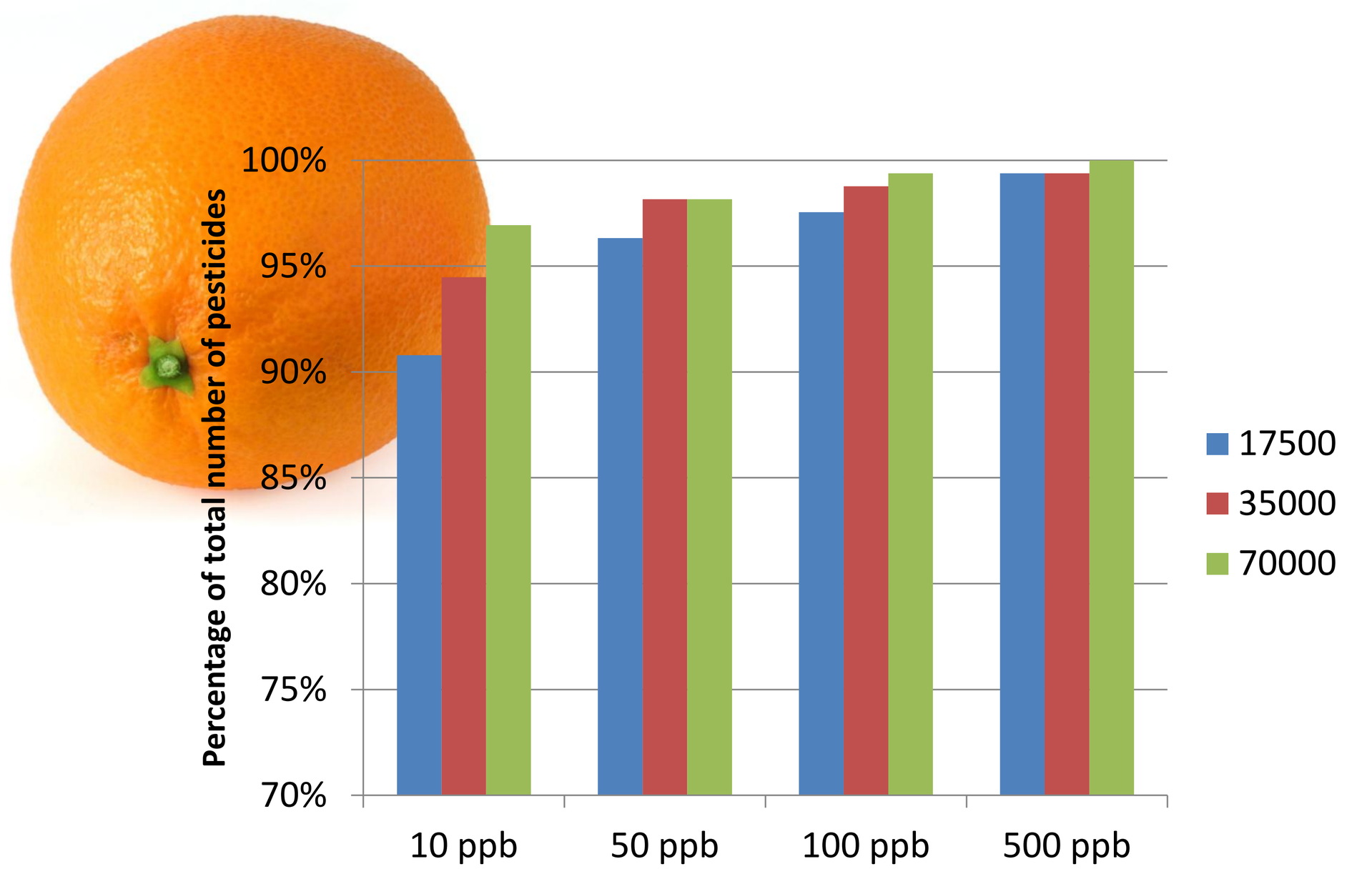


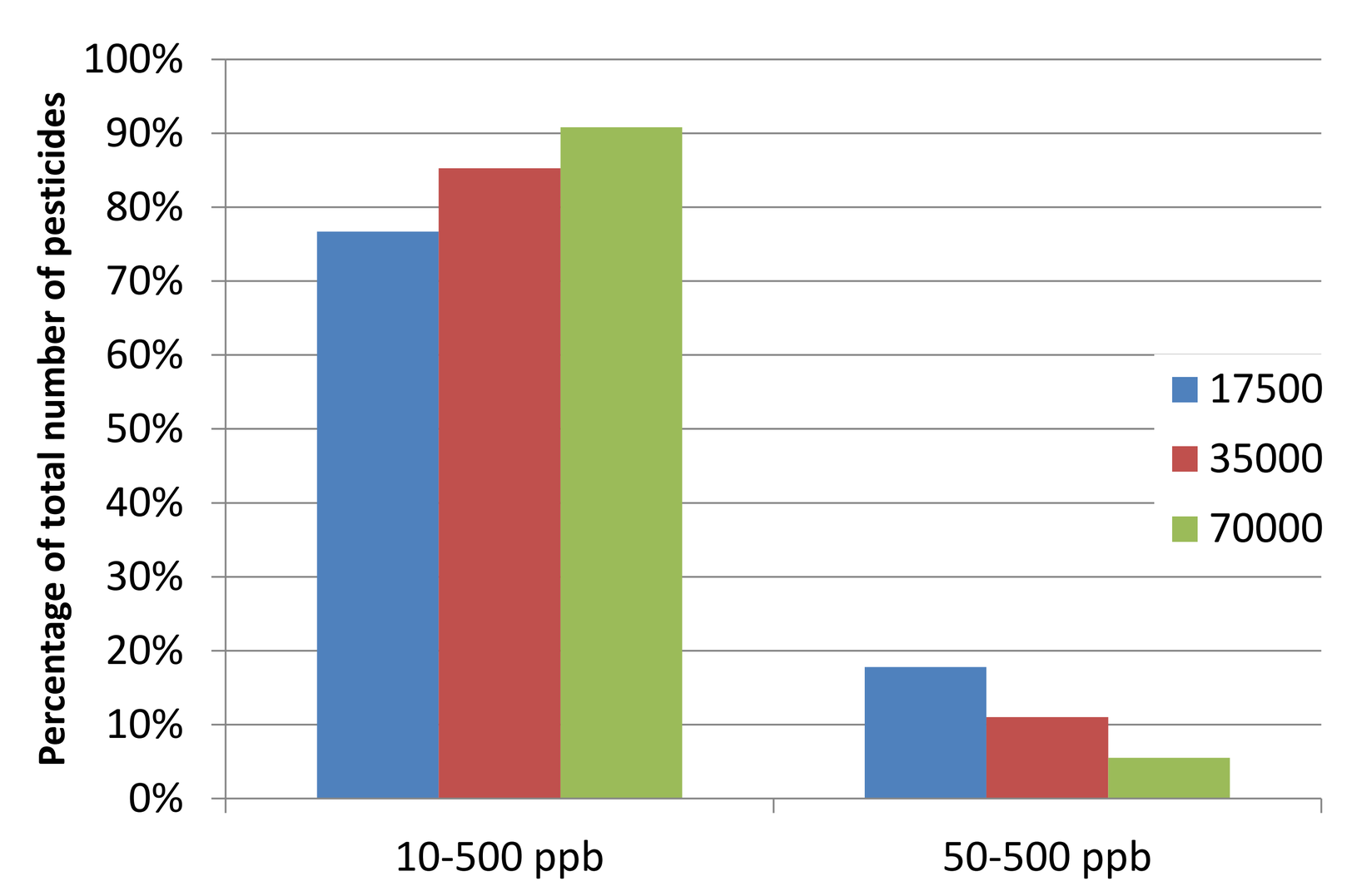


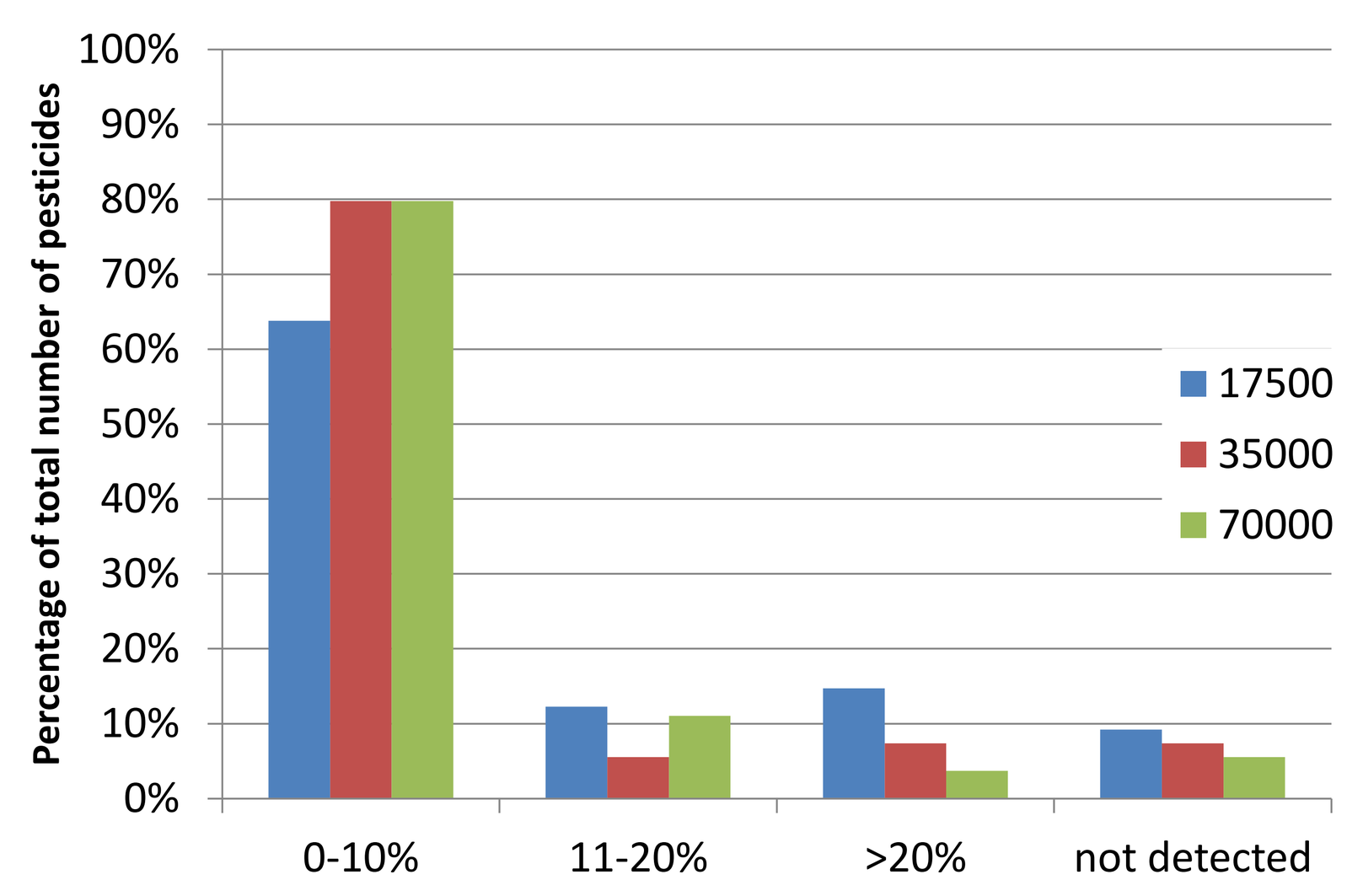


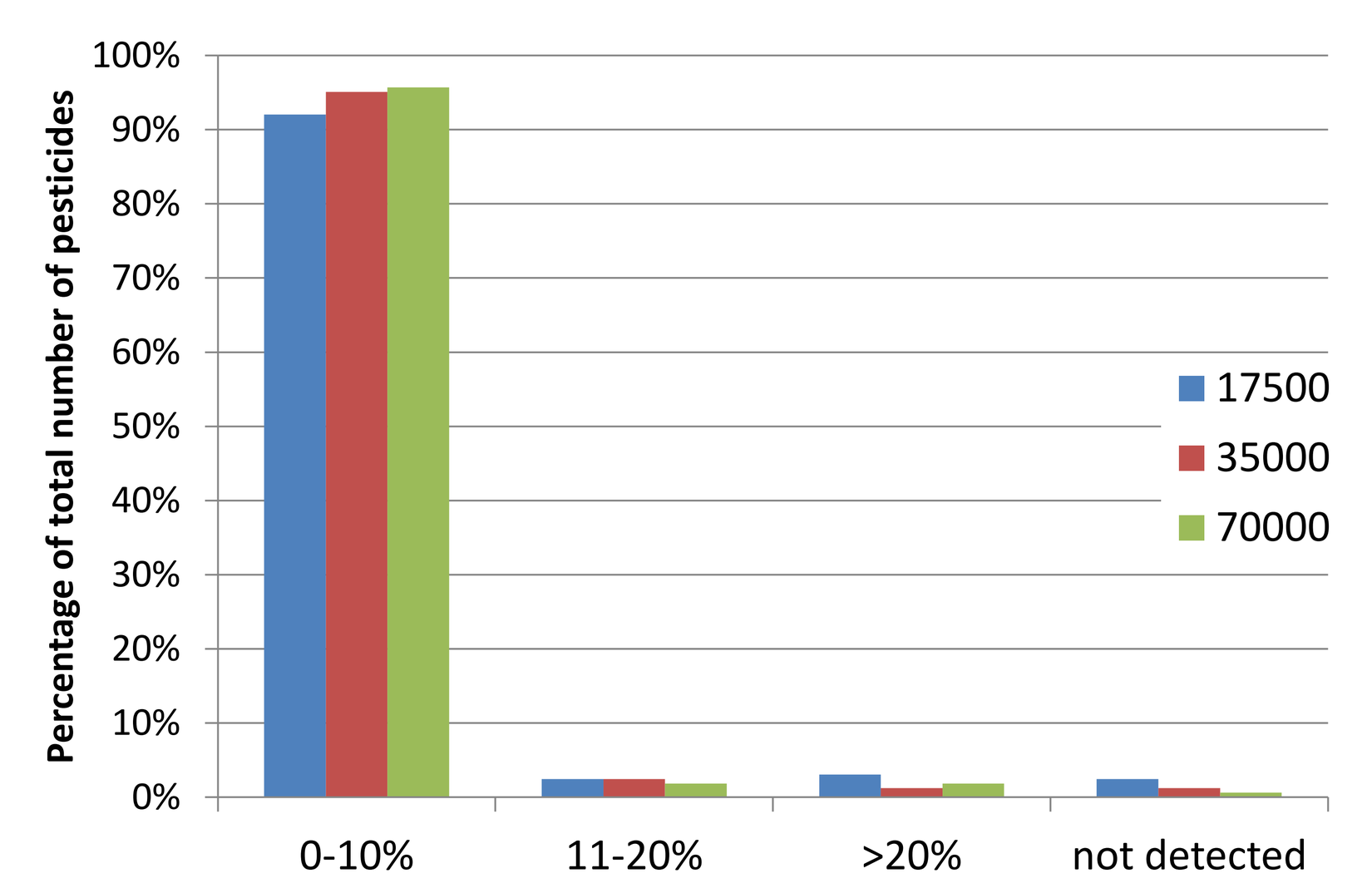


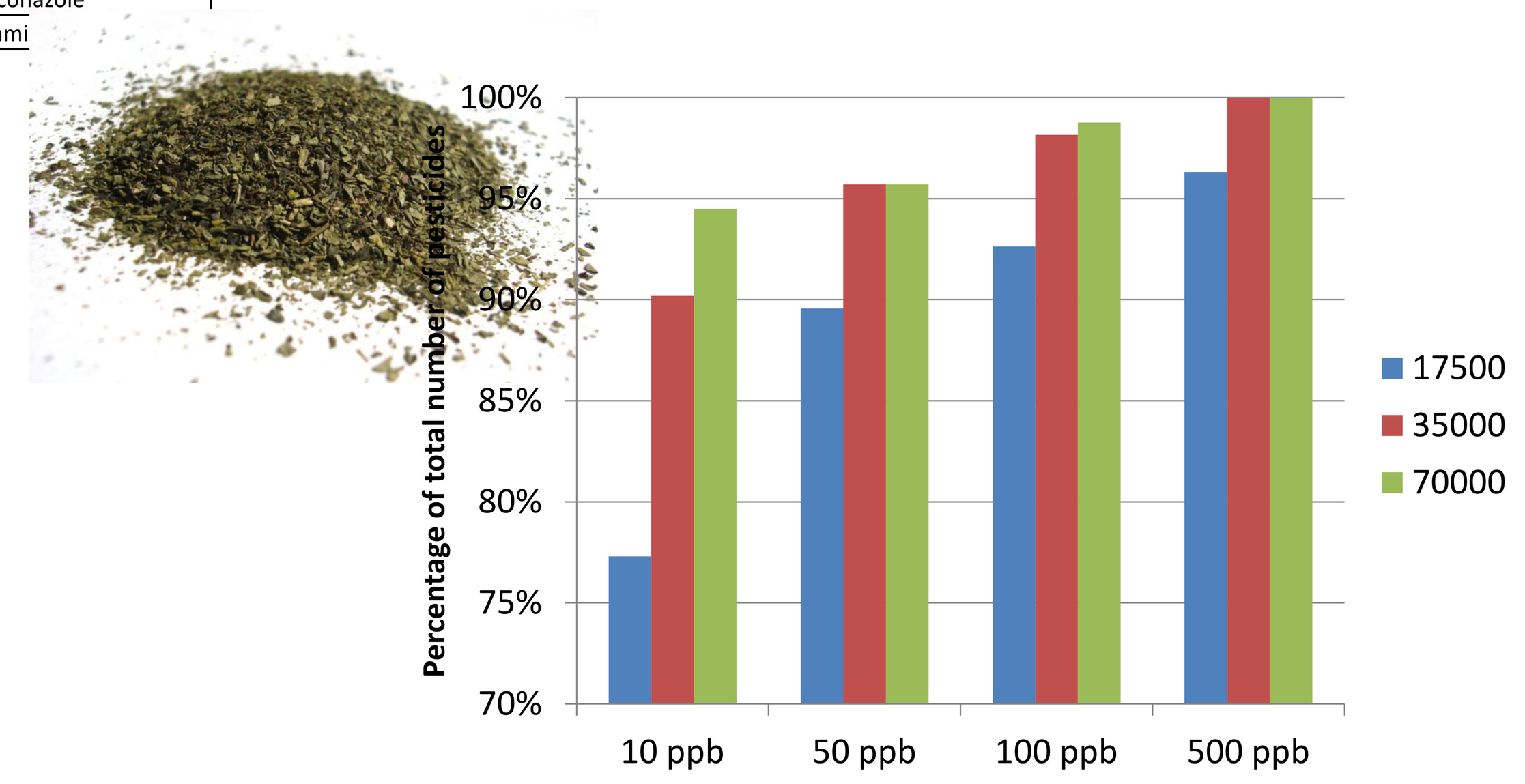


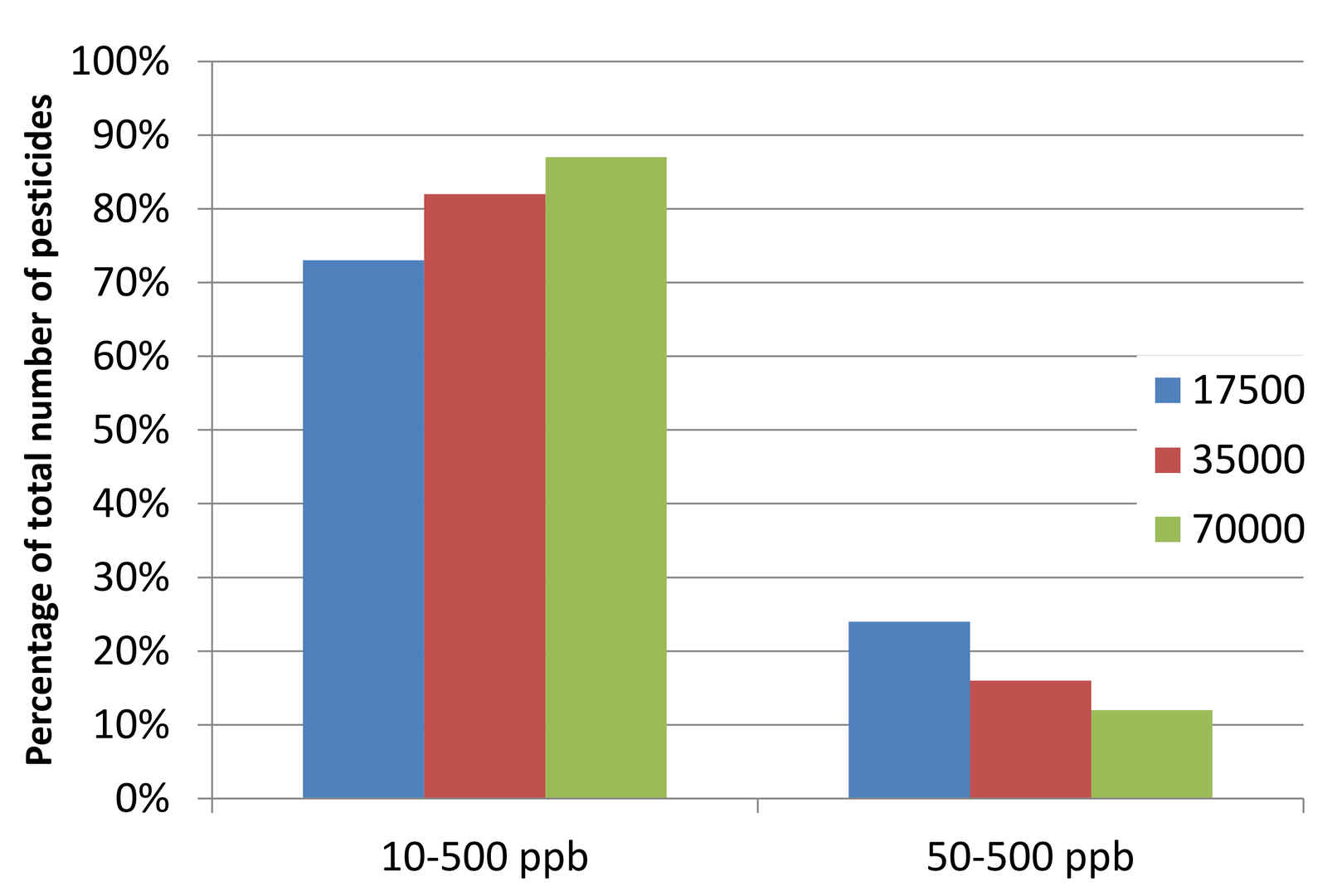


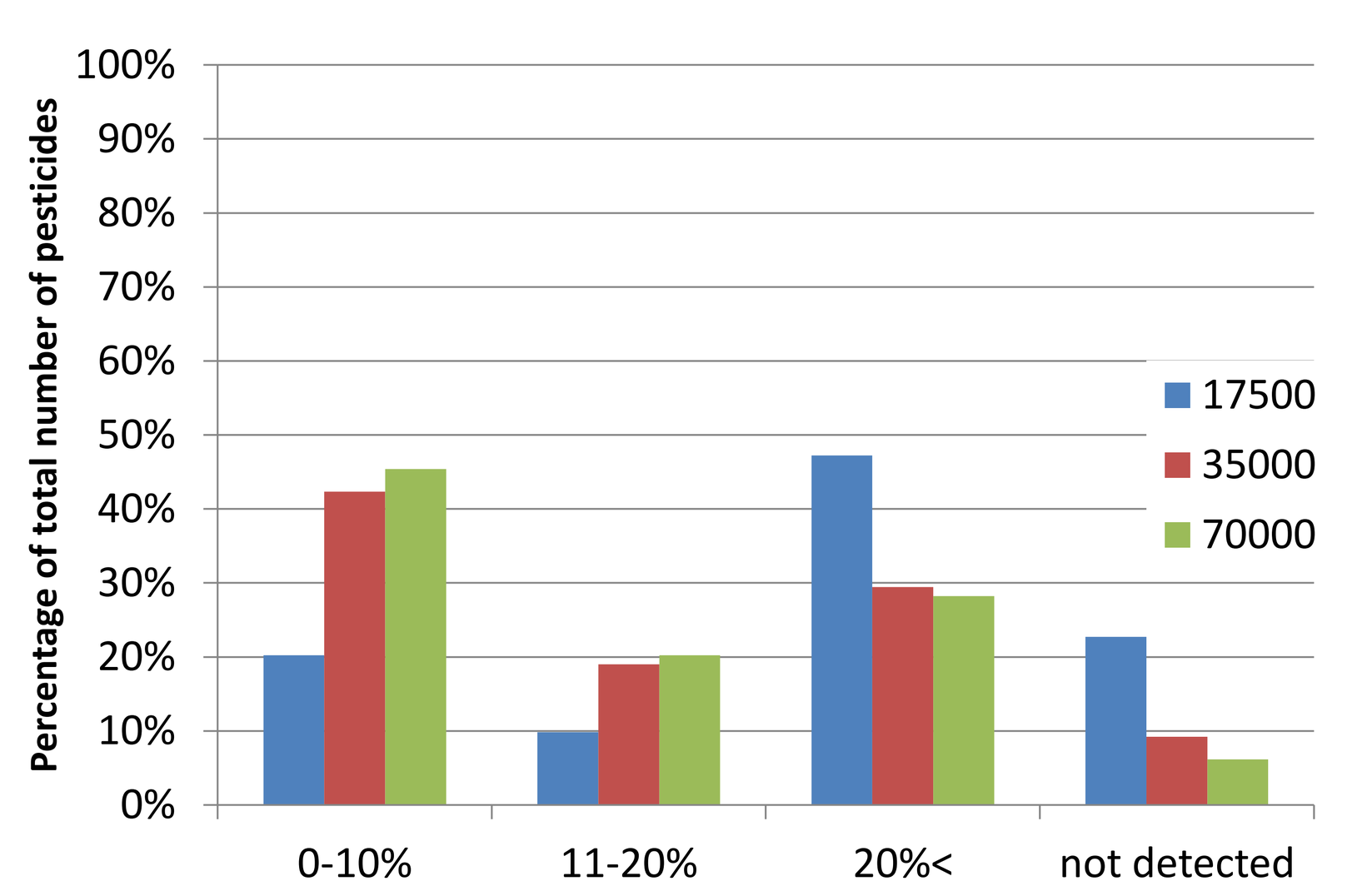


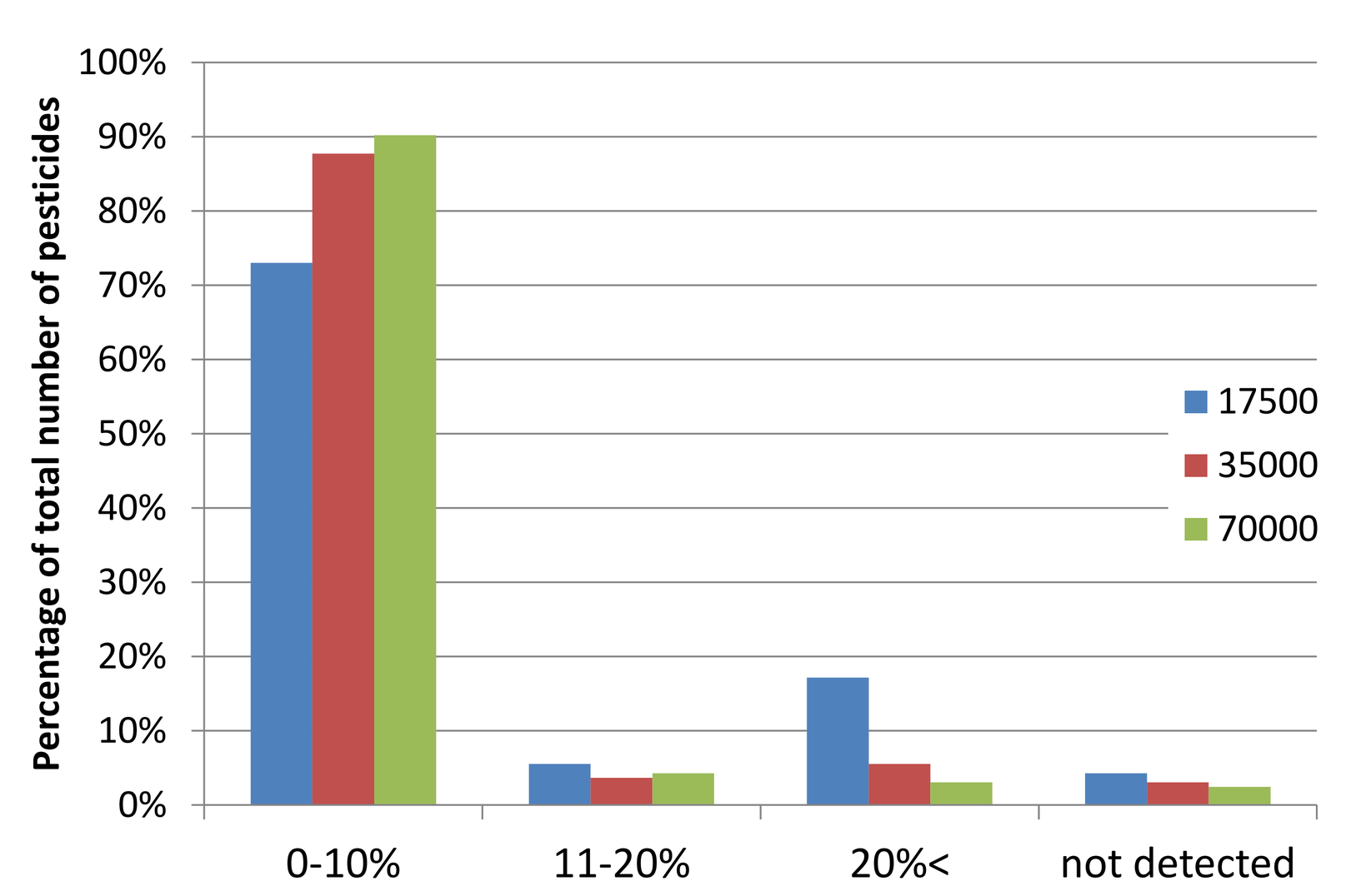












CONCLUSIONS

- Carried out experiments demonstrated usefulness of Orbitrap in pesticide analysis.
- Increase of resolution improved limit of detection and repeatability of peak area. Resolution of 35000 was sufficient to detect (with mass tolerance of 5 ppm) 95% of analysed pesticides in tomato, pepper and orange.
- To obtain good repeatability of peak area at level 10 ppb resolution of 35000 or 70000 was required.
- High sensitivity of the QExactive sectrometer allowed to dilute samples 5 times. This dilution reduced potential matrix effects.

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