3rd National Environment and Health Action Plan (NEHAP) Conference 2017

ORGANOPHOSPHORUS PESTICIDES CONTAMINATION IN SURFACE WATER OF THE LANGAT RIVER, SELANGOR, MALAYSIA

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Common pesticide use

- Agricultural production
- Public health control (e.g. malathion for malaria control)
- Commercial applications (e.g. triclosan as a water disinfectant)
- Home use (e.g. insect repellent)

→ **Increased pesticide use**

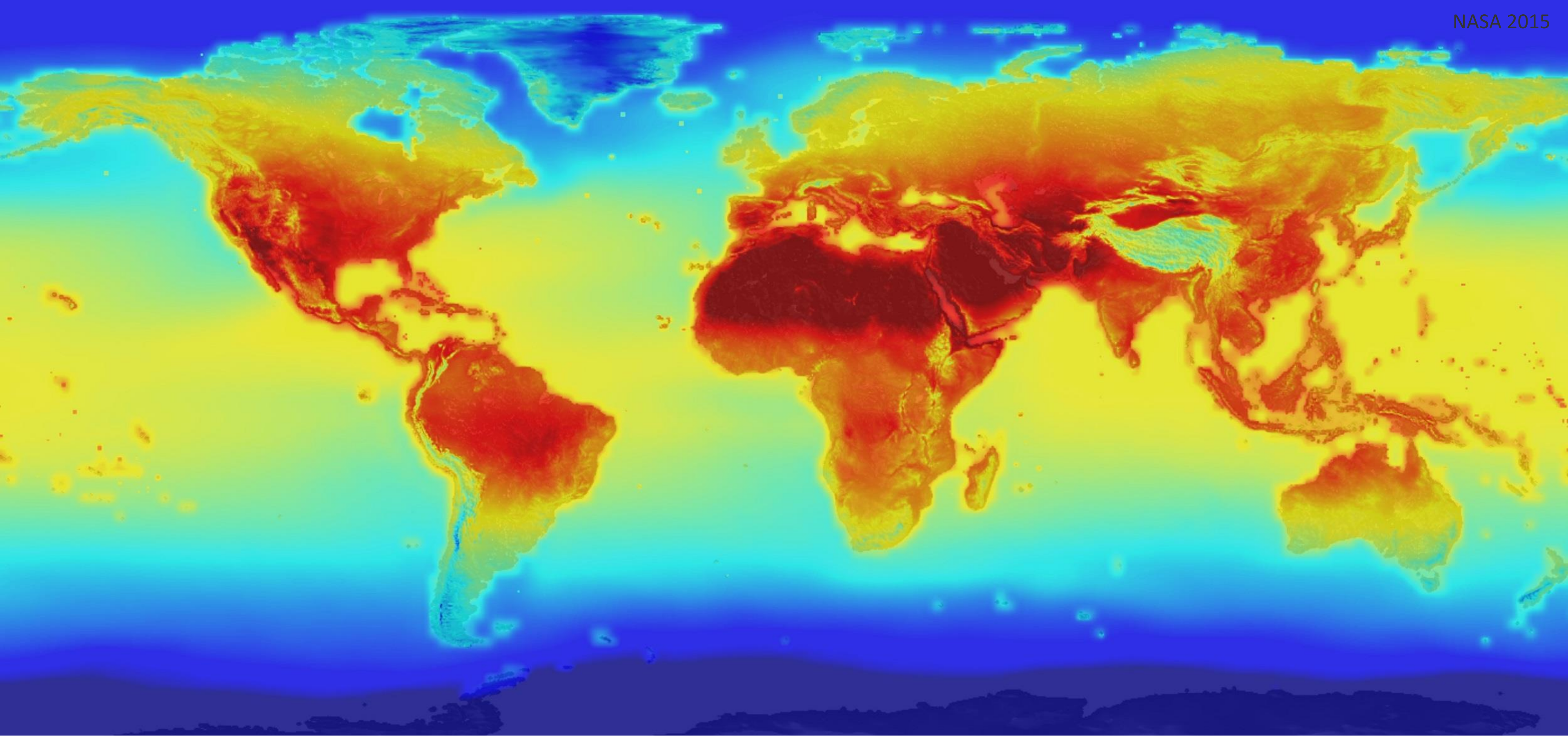
Extraneous factor – Climate change

- Bring about ubiquitous sources and increased impacts of pesticides in the environment.

Enhanced pest activity → Rapid reproducing → Spread after floods → Increased vector-borne virus

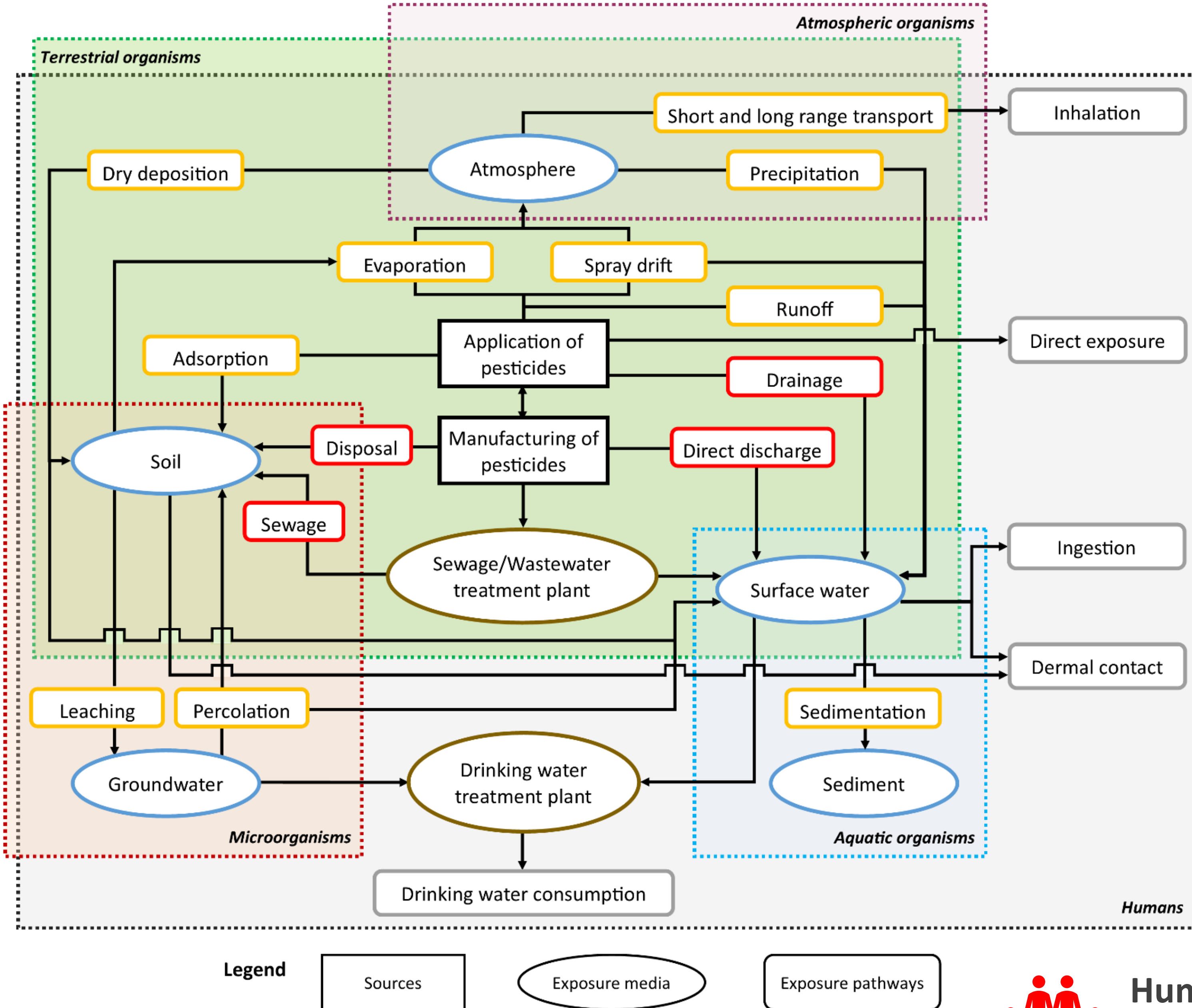
Increased temperature, precipitation and humidity → Poorly dried crops → Mycotoxin produced → Production affected

→ **Increased pesticide use**



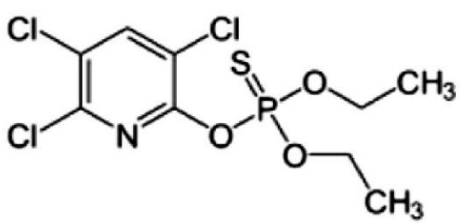
- Based on Chiu et al. (2017), the future increase in pesticide use was projected based on the increasing atmospheric temperature.
- Altered rainfall pattern - Higher impacts were predicted in the less intensive agricultural areas.
- Continuous environmental distribution and toxicity of pesticides, due to the affected
  - Physical (e.g., altered temperature and wind pattern)
  - Chemical (e.g., degradation and transformation)
  - Biological (e.g., changes in soil and water microbial activity) (Noyes et al., 2009).

Ecological changes

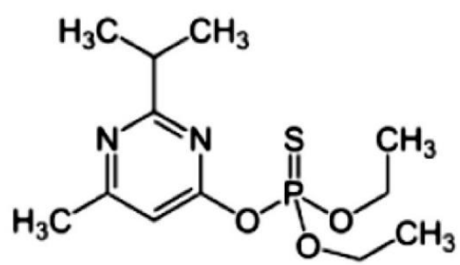


Human health impacts

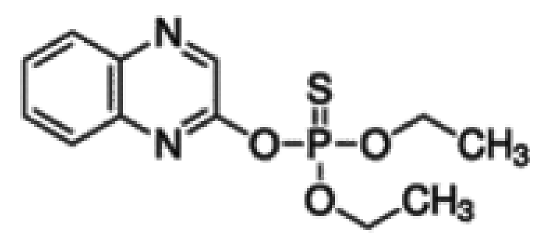
- Currently, several pesticides have been listed as endocrine disrupting compounds (EDCs) due to their modes of action and mechanisms in endocrine system disruption (Mnif et al., 2011).
- Organophosphorus pesticides (OPPs) are the synthetic pesticides;
  - Contain organophosphate compounds.
  - Mainly used as insecticides.
  - Popular alternative to organochlorine pesticides (OCPs) in the late 1990s after several persistent OCPs were banned.
- OPPs are acetylcholinesterase (AChE) inhibitors high toxicity, carcinogenicity and neurotoxicity (Walker et al., 2012; Gilden et al., 2010; Liu and Lin, 2005; Alavanja et al., 2004).



Chlorpyrifos

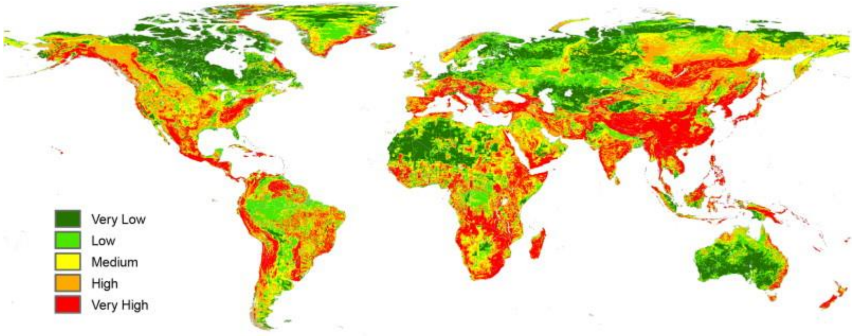


Diazinon

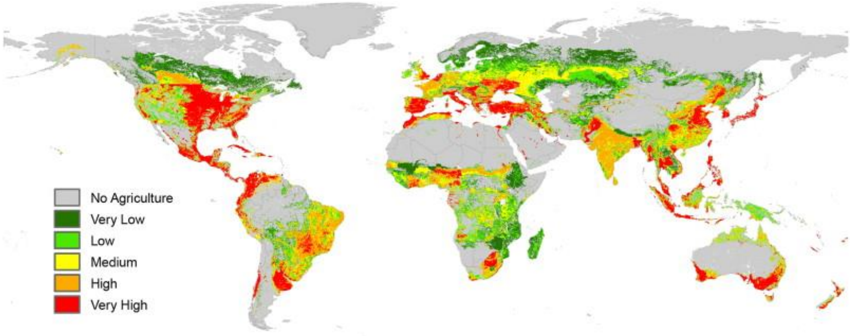


Quinalphos

- Worldwide determination, mainly due to their high production and application of pesticides.
  - Spain (Campo et al., 2013; Köck-Schulmeyer et al., 2013);
  - U.S. (Stone et al., 2014);
  - China (Gao et al., 2009);
  - India (Mohammed and Penmethsa, 2014; Singh et al., 2015).



Map 1: Global insecticide runoff vulnerability map.
(Ippolito et al., 2015)



Map 2: Global insecticide runoff hazard map.
(Ippolito et al., 2015)

- In Malaysia, moderate loadings of OPP chlorpyrifos was identified and correlated to the agricultural activities (Osman et al., 2012; Zubir et al., 2014).

Langat River, Selangor, a main river located at the most populated and urbanized river basin in Malaysia with rapid land use change.

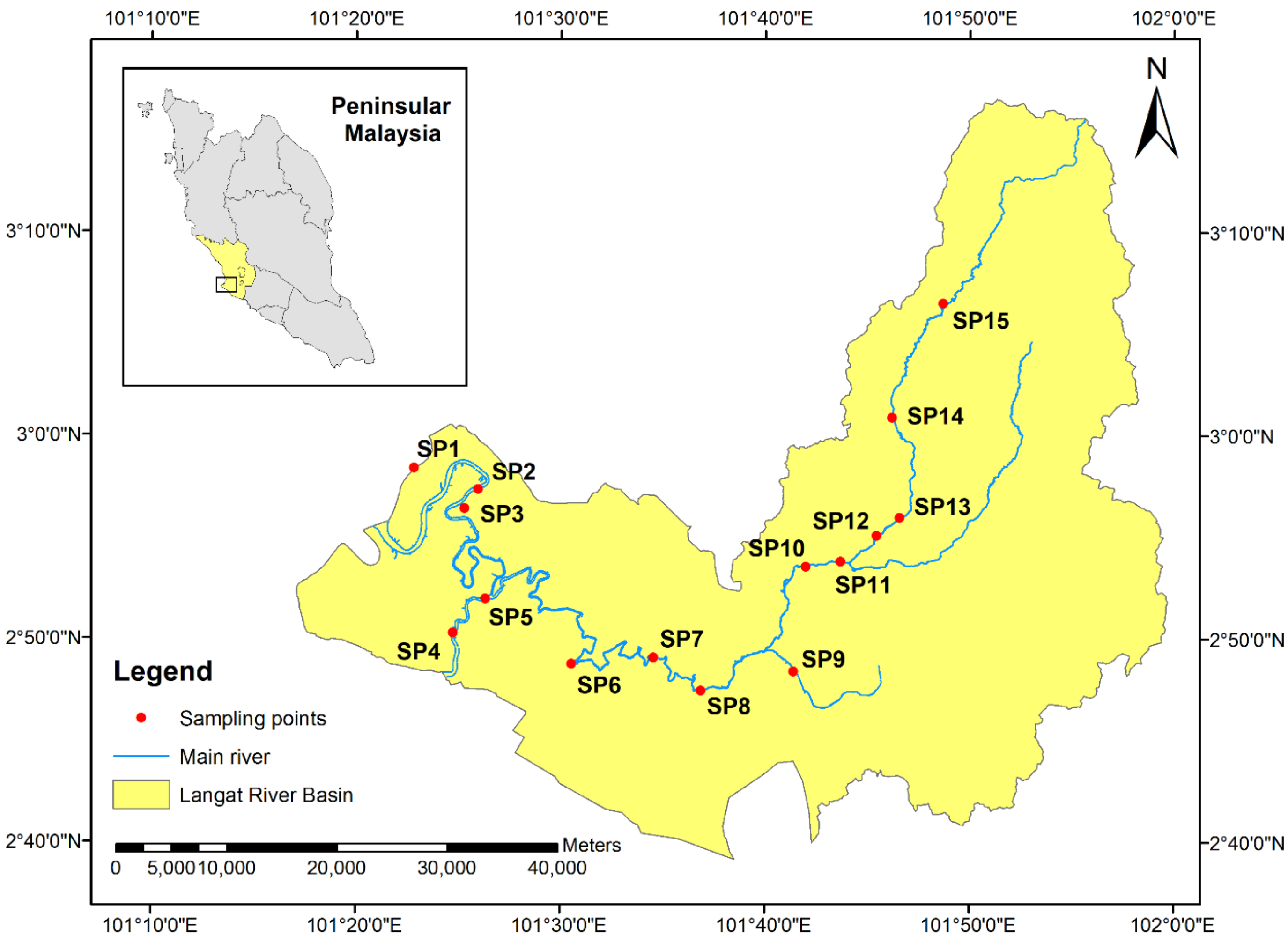


Figure 1 Map of the sampling points in the Langat River Basin.

Method development

- Analytical method development.
  - Solid phase extraction.
  - Instrumental chromatographic separation.
- Developed and optimised analytical method.
  - Solid phase extraction and high performance liquid chromatography coupled with diode array detector (SPE-HPLC-DAD).
- Validated analytical method.

SPE-HPLC-DAD

Accuracy – Spike recovery
- Quinalphos = 100.21%
- Diazinon = 100.15%
- Chlorpyrifos = 32.40%

Precision - Inter-day reproducibility and intra-day repeatability
- Relative standard deviation < 20.00%

Sensitivity – Correlation coefficient of calibration curve
- Quinalphos = 0.9999
- Diazinon = 0.9998
- Chlorpyrifos = 0.9997

Limits of detection (LOD)
- Instrument detection limit = 0.250 mg/L
- Method detection limit
  - Quinalphos = 0.003 µg/L
  - Diazinon = 0.003 µg/L
  - Chlorpyrifos = 0.006 µg/L

Solid phase extraction (SPE)

- Solid phase extraction (SPE) method was modified and optimised from the method reported by Sanagi et al. (2011).
  - Step
  - Solvent type
  - Solvent volume

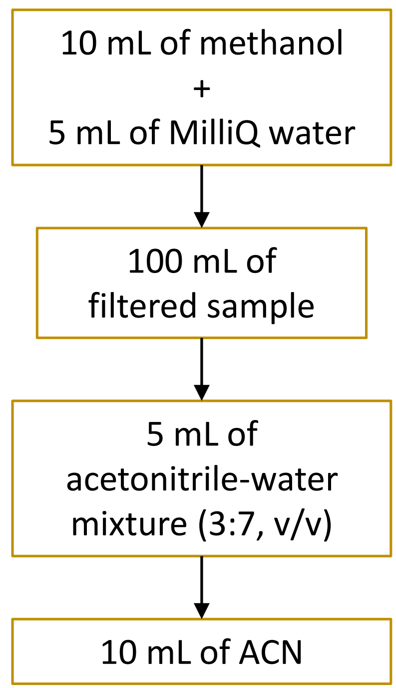


Figure 2 Flow chart and summary of sample extraction and enrichment for the instrumental analysis of surface water concentration and distribution of OPPs.

Instrumental chromatographic separation

- Multiresidues were analysed by using HPLC Agilent Series 1200, coupled with diode array detector (HPLC-DAD).
- Zorbax SB-C18 column was chosen with the developed and optimised HPLC chromatographic condition.
- Optimisation was done to achieve highest signal intensities and symmetries.

Table 1 Optimal chromatographic condition for the determination and quantification of OPPs.

Chromatographic condition	
Instrument	HPLC Agilent Series 1200
Detector	Diode array detector
Column	Zorbax SB-C18 4.6 mm × 250 mm
Injection volume	30 µL
Mobile phase	40% H_2O (A) and 60% ACN (B)
Elution	Isocratic
Column temperature	30 ˚C
Flow rate	1.5 mL/min
Run time	16 min
Wavelength	210 nm
Working environment	87 bar

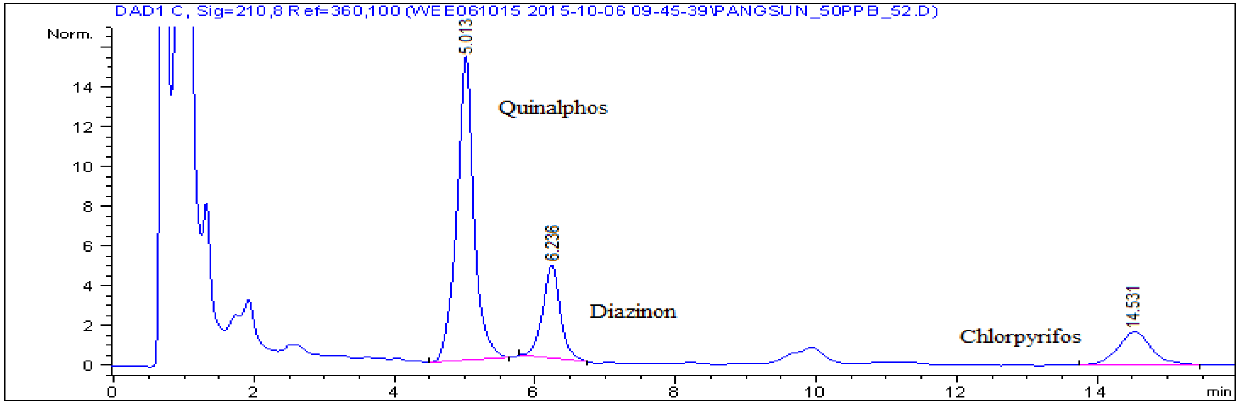


Figure 3 Chromatogram of OPPs separation in a single analytical run of spiked (50 µg/L) river water.

Occurrences and distribution of OPPs

Table 2 Occurrences and distribution of OPPs in water samples (*n* = 15) at Langat River with duplicate analyses (*n* = 2) for each sampling point.

Sampling point	**Mean concentration in the surface water (µg/L) and (SD)**		
	Quinalphos	Diazinon	Chlorpyrifos
SP1	< MDL	< MDL	0.0204 (0.0289)
SP2	0.0201 (0.0284)	< MDL	0.0184 (0.0260)
SP3	0.0640 (0.0133)	0.0132 (0.0186)	0.0442 (0.0094)
SP4	0.0115 (0.0162)	< MDL	0.0277 (0.0391)
SP5	0.0257 (0.0000)	< MDL	0.0407 (0.0003)
SP6	0.0352 (0.0498)	0.0372 (0.0526)	0.0512 (0.0204)
SP7	0.0126 (0.0178)	0.0296 (0.0418)	< MDL
SP8	< MDL	< MDL	< MDL
SP9	0.0301 (0.0064)	< MDL	< MDL
SP10	< MDL	< MDL	< MDL
SP11	< MDL	< MDL	< MDL
SP12	< MDL	< MDL	< MDL
SP13	0.0206 (0.0291)	< MDL	< MDL
SP14	0.0335 (0.0102)	0.0316 (0.0070)	0.0326 (0.0107)
SP15	0.0135 (0.0191)	0.0292 (0.0058)	0.0676 (0.0236)
% of detection	66.67	33.33	53.33
Min	0.0000	0.0000	0.0000
Max	0.0640	0.0372	0.0676
Mean	0.0178	0.0094	0.0202
SD	0.0181	0.0145	0.0228

MDL method detection limit (quinalphos = 0.003 µg/L; diazinon = 0.003 µg/L; chlorpyrifos = 0.006 µg/L)

- All the three OPPs were found in Langat River.
- This study was also first to reveal concentration of quinalphos and diazinon in Langat River, Selangor.

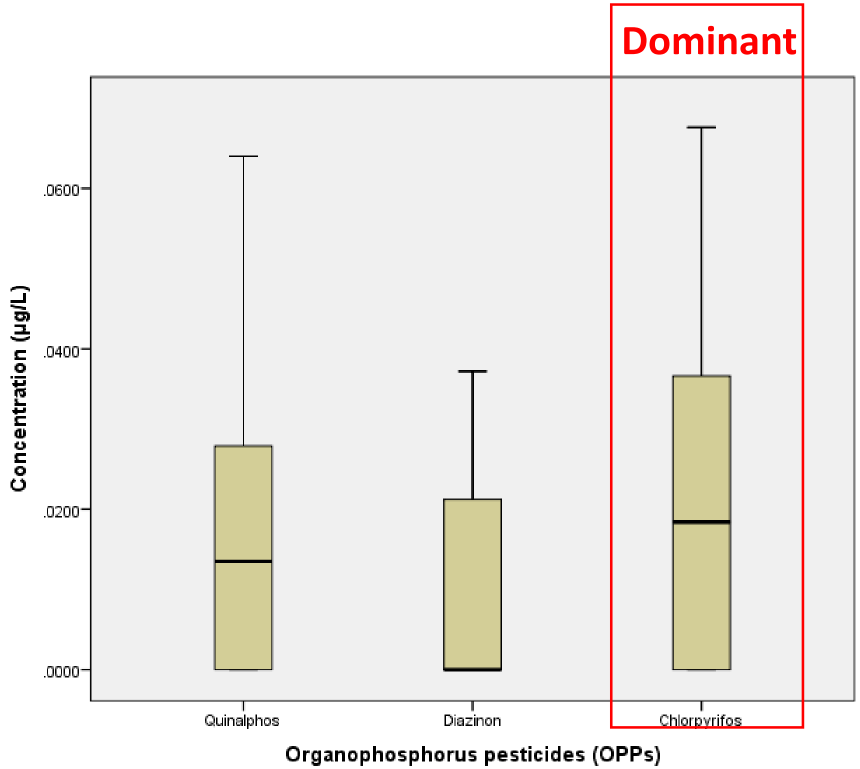


Figure 4 Boxplot for occurrence of OPPs in Langat River Basin.

Low dispersion along Langat River

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MDL method detection limit (quinalphos = 0.003 µg/L; diazinon = 0.003 µg/L; chlorpyrifos = 0.006 µg/L)

- Relatively low mean concentration of chlorpyrifos, compared to previous study done by Osman et al. (2012) - Changes in application of pesticides in the Langat River Basin.

Urban discharges, attributed to the absence of a wastewater treatment system in regulating organic pollutants.

- WWTP discharge
- domestic wastewater
- industrial effluents

Residential area with crops plantation and illegal waste dumping activities.

- domestic wastes
- plantation effluent
- leachate of wastes

Pesticides move offsite into surface waters through runoff, drainage or leachate.

5.057 µg/L with SD value 3.623 (Osman et al., 2012)

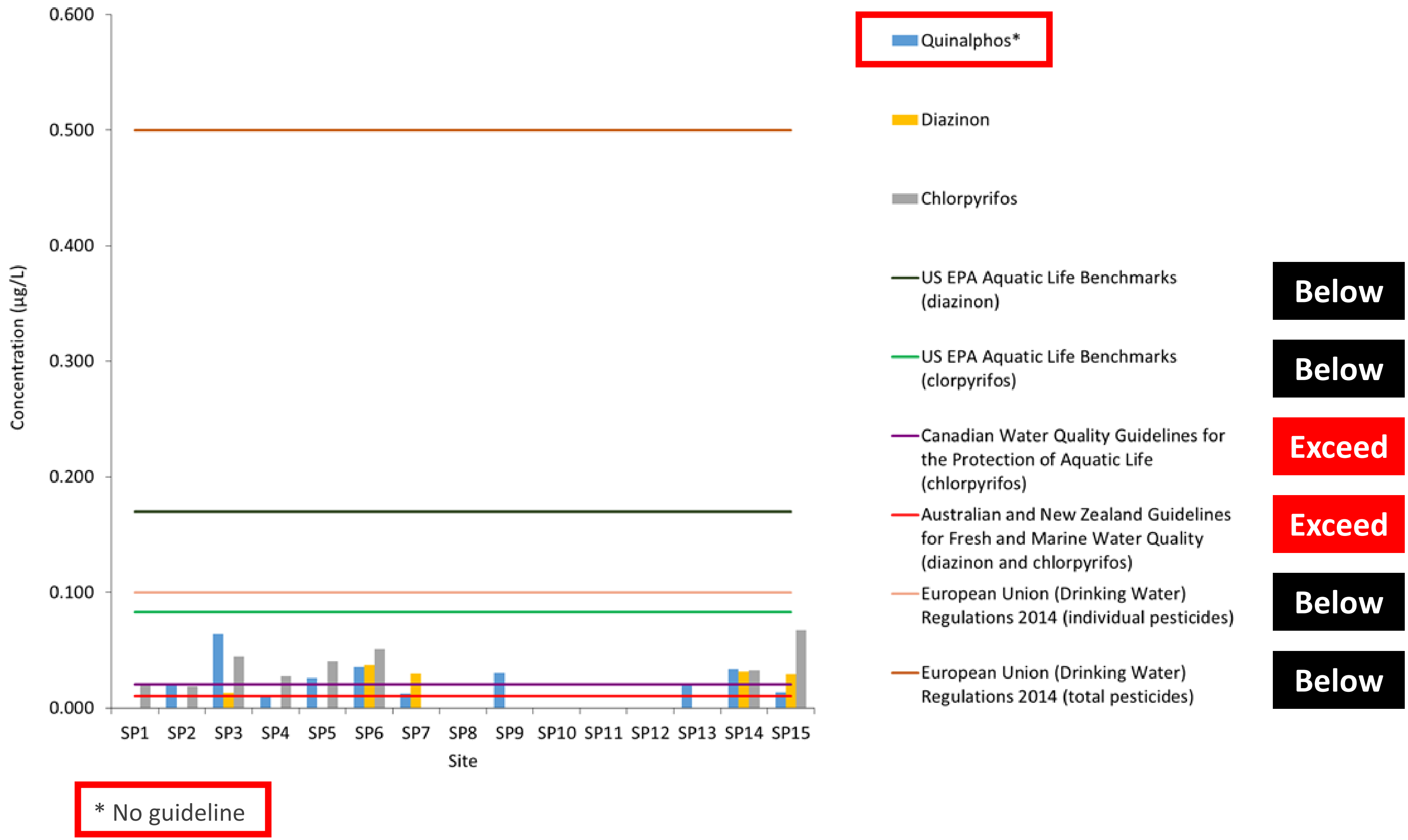

Figure 3 Distribution of quinalphos, diazinon and chlorpyrifos in surface water of Langat River, compared to

(i) trigger values established under United States Environmental Protection Agency (US EPA) Aquatic Life Benchmarks (diazinon = 0.010 µg/L; chlorpyrifos = 0.010 µg/L),

(ii) limit of Canadian Water Quality Guidelines for the Protection of Aquatic Life (chlorpyrifos = 0.020 µg/L),

(iii) criteria maximum concentration (CMC) established under Australian and New Zealand Guidelines for Fresh and Marine Water Quality (diazinon = 0.170 µg/L; chlorpyrifos = 0.083 µg/L) and

(iv) maximum contamination level (MCL) of individual pesicides (0.100 µg/L) and total pesticides (0.500 µg/L) under European Union (Drinking Water) Regulations 2014.

Conclusion

An optimized & validated analytical method (SPE-HPLC-DAD).

Challenges – Multiresidues determination in a single analytical run.

A baseline data – OPPs contamination in Langat River.

Preliminary screening of risk is vital for sustainability of riverine ecosystems.

Potential ecological & human health risk.

A supportive tool in environmental quality & human health protection.

A principal basis of decision making in the legislative & policy ratification – Integration of organic pollutants regulation into the existing legislative & policy framework.

THANK YOU

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