

Supplementary information for

**Tebuconazole and terbuthylazine encapsulated in nanocarriers:
preparation, characterization and release kinetics.**

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Fig. 1S.

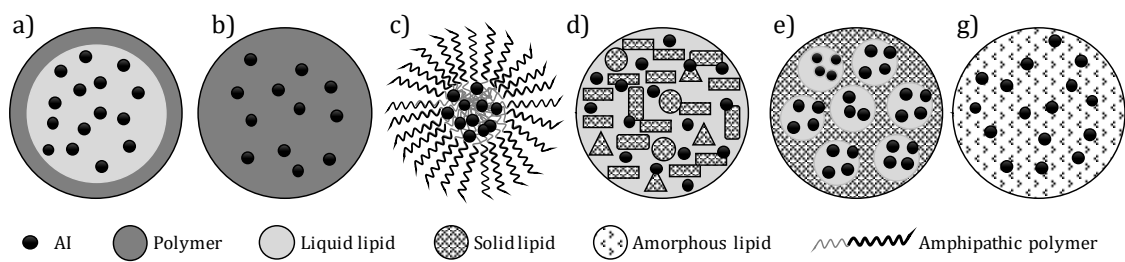
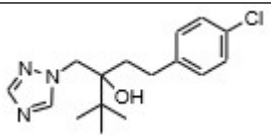
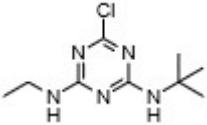


Fig. 1. Schematic presentation of different nanoparticle structures: a) nanocapsule, b) nanosphere, c) nanomicelle, d) imperfectly structured solid matrix, e) solid matrix containing nano-compartment of oil, and f) structureless solid amorphous matrix (modified from^{1,2}).

Table S1. Main physicochemical properties and chemical structure of tebuconazole (TBZ) and terbuthylazine (TBA) from Pesticides Properties Data Base³

	M_w^a (g mol ⁻¹)	S_w^b (mg l ⁻¹)	Log K_{ow}^c	P_v^d (mPa)	H^e (Pa m ³ mol ⁻¹)	Chemical structure
TBZ	307.8	36.0	3.7	0.0013	1×10^{-5}	
TBA	229.7	6.6	3.4	0.152	2.3×10^{-3}	

^a M_w : molecular mass

^b S_w : solubility in water at 20 °C

^c K_{ow} : octanol-water partition coefficient at pH 7, 20 °C

^d P_v : vapor pressure at 20 °C

^e H: Henry's law constant at 25 °C

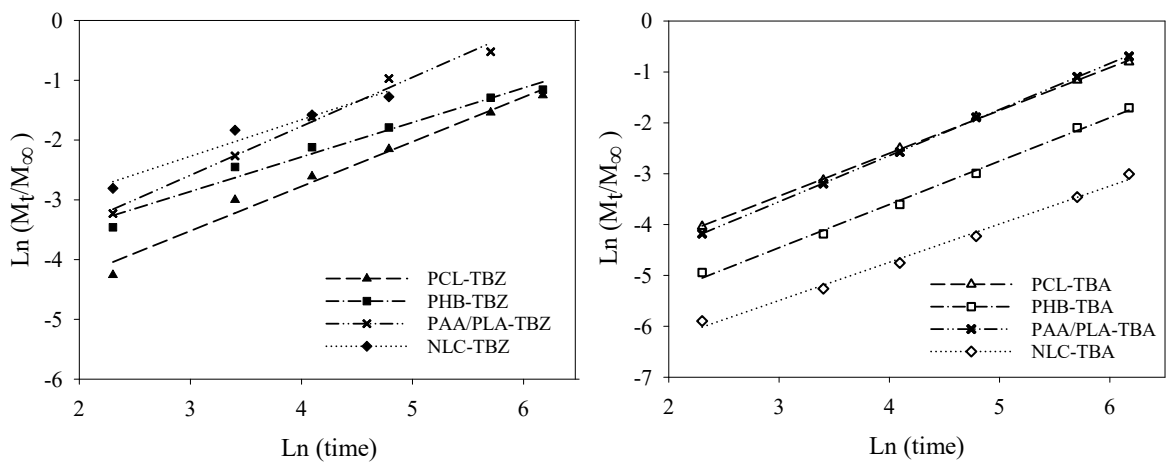


Fig. S2. Plot of the logarithm of tebuconazole (TBZ) and terbuthylazine (TBA) released from poly- ϵ -caprolactone (PCL), poly(3-hydroxybutyrate (PHB) and poly(acrylic acid)/polylactide (PAA/PLA) and nanostructured lipid nanocarrier (NLC) as a function of the logarithm of time, according to Korsmeyer-Peppas model.

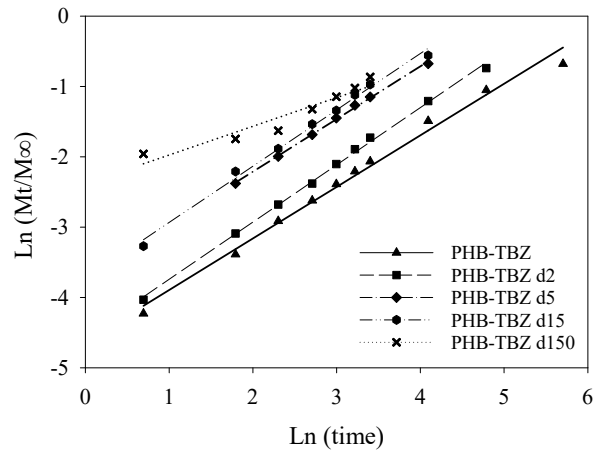


Fig. S3. Plot of the logarithm of tebuconazole (TBZ) released from poly(3-hydroxybutyrate (PHB) undiluted and diluted 2, 5, 10 and 100 times as a function of the logarithm of time, according to Korsmeyer-Peppas model.

LC-MS/MS analysis.

HPLC analysis was performed using an Agilent 1200 chromatographic system (Agilent, Santa Clara, CA, USA) equipped with a vacuum degasser, binary pump, autosampler and a column thermostat, which was connected online to an ESI/QqQ mass spectrometer Agilent Triple Quad 6410 (Agilent, Santa Clara, CA, USA). The chromatographic/mass spectrometric system was controlled by Mass Hunter software. The HPLC conditions were as follows: ACE 3 C18 chromatographic column 150 mm in length x 2.2 mm internal diameter and 3 μm particle size, with integrated guard column 20 mm in length x 2.2 mm internal diameter and 3 μm particle size (ACE, Scotland, UK). The column temperature was maintained at 30 °C. The mobile phase consisted of 0.1% acid formic (98% Sigma-Aldrich, Germany) in water and acetonitrile. The mobile phase gradient was as follows: 0–1 min 10% B, 1–7 min from 10% B to 98% B, and 98% B held to 12 min, 12–13 min from 98% B to 10% B with a subsequent equilibration step of 10% B to 25 min. The flow of mobile phase was 0.3 ml/min during all the analyses.

The injection volume was 5 μl of the samples and 5 μl of the instrumental standard solution (d-metolachlor in acetonitrile, 50 ng ml⁻¹; Dr. Ehrenstorfer).

The mass spectrometer was operated in the ESI-positive SRM mode (gas temperature 350 °C, gas flow 9 l min⁻¹, nebuliser gas 40 psi, capillary voltage 4.0 kV). The following ion transitions were monitored: tebuconazole, m/z 308.2→70.0 with a collision energy of 20 eV (and for confirmation, m/z 308.2→151.0, 20 eV); terbuthylazine, m/z , 230.0→174.0, 20 eV (m/z 230.0 →104.0, 20 eV); D-metolachlor, m/z 290.1→258.1, 10 eV (m/z 290.1→182.1, 10 eV).

Quantitation of analytes was performed using an internal standard calibration method. Internal standards (d-metolachlor) were added to all samples for these purposes. Good linearity of calibration curves was obtained across the whole concentration range (from 1 to 1000 ng ml⁻¹).

References

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- 3 K. A. Lewis, J. Tzilivakis, D. J. Warner and A. Green, *Hum. Ecol. Risk Assess.*, 2016, **22**, 1050–1064.