Supplementary information to: Analysing organic micropollutant accumulation in closed loop FO-RO systems: a pilot plant study

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1. SPE protocol

In order to concentrate analytes and remove salts from the extracts to be analyzed by U-HPLC-HRMS, feed and draw solution samples were subjected to Solid Phase Extraction (SPE). A calibration series was constructed consisting of 11 samples between 0.05 and 40 µg/L in approximately log2 dilution (concentrations on lower end were rounded off for pipetting). All SPE samples, both experimental samples and calibration series, were spiked with the same internal standards, the identity and concentrations of which are specified in Table 1. An identical calibration series was included for each SPE run, yielding 3 identical calibration series.

Water samples were stored refrigerated prior to SPE. Before starting SPE, samples were equilibrated to room temperature and briefly degassed using vacuum. Degassing was done in order to avoid the formation of air bubbles in the adsorbent bed, which decreases extraction efficiency. Oasis HLB 10 cc SPE cartridges (Waters, MA, USA) were attached to a SPE vacuum manifold and were wetted using 2 mL HPLC-quality MeOH and vacuum, followed by 10 mL Milli-Q. Subsequently, samples were loaded onto the SPE cartridges using siphons (Waters, USA). Sample flow rate was controlled using the vacuum manifold. Once the samples had completely passed through the SPE cartridges, flow was stopped while maintaining a wetted adsorbent bed. The cartridges were then washed using 10 mL Milli-Q, in order to remove inorganic salts. Once washing was complete, all remaining water was sucked out of the cartridges using the vacuum

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Table 1: Internal standards used for OMP quantification

Internal standard	Concentration (µg/L)
Metoprolol-D7	150
Atrazine-D5	4
Diuron-D6	12
Paracetamol-D4	30
Sulfamethoxazole-13C6	60
Ketoprofen-D3	60

manifold, and cartridges were air-dried for 10 minutes using air flow. Subsequently, the manifold was fitted with sample vials under the SPE cartridges, and analytes were eluted using 2 times 4 mL MeOH of HPLC quality, yielding 8 mL eluens. In the case of the RO permeate samples, the SPE concentrate was further concentrated by partial evaporation of the MeOH samples to a final volume of 1 mL. This was also done for the calibration series used for the quantification of the RO permeate samples

2. HPLC-HRMS protocol

OMPs were analysed using UHPLC-HR-Orbitrap-MS (benchtop Exactive Orbitrap, Thermo-Fisher Scientific, USA). An Accela autosampler, maintained at 15 °C, was coupled to an Accela degasser and an Accela 1250 pump. The injected extract (10 µL) was separated on a Nucleodur C18 Pyramid column (100 x 2 mm, 1.8 µm; Macherey-Nagel, USA) at a constant flow of 300 µL/min. Solvents A (0.08% HCOOH in ultrapure water) and B (MeOH) were used in the following gradient: 1 minute isocratically at 98% A and 2% B, increase of B to a composition of 10% A and 90% B during 3.5 minutes, increase of B to a composition of 100% B during 2 minutes, 1.5 minutes isocratically at 100% B and finally the column was equilibrated for 1.5 minutes at the initial conditions of 98% A and 2% B. Components were ionized with a H-ESI-II (Heated Electrospray ionization) interface. The sheath gas flow rate was set to 30 arbitrary units, no auxiliary gas or sweep gas was used. The spray voltage, capillary voltage, tube lens voltage and skimmer voltage was set to 4000 V, 82.5 V, 120 V and 20 V respectively for positive ionization mode, and 4000 V, -30 V, -95 V and -26 V respectively for negative ionization mode. The capillary temperature was set to 250 °C and the vaporizer heater temperature was set to 350 °C. Detection occurred with an Orbitrap high resolution mass spectrometer, working alternatively in positive and negative modes at a switching rate of 2 Hz. The resolution was set to 50000 full width at half maximum, an automatic gain control target of 5.105 was used, and the scan range was 100.00 – 700.00 m/z. The high energy collision dissociation cell was turned off. Analysis data was processed with the Thermo Xcalibur 2.1.0.1140 package. Analytes were interpreted according to their accurate precursor ion masses: [M+H]+. The maximum mass tolerance was set to 5.0 ppm.

3. OMP concentrations during NaCl DS experiment

Below are the OMP concentrations in the FO feed, diluted and concentrated draw solution and RO permeate obtained using NaCl as draw solute. Solid lines

are fits of Eq. 11, in all cases except RO permeate where points are joined by straight line segments. Where the RO permeate data is missing in a plot indicates that said OMP was not detected in the RO permeate.

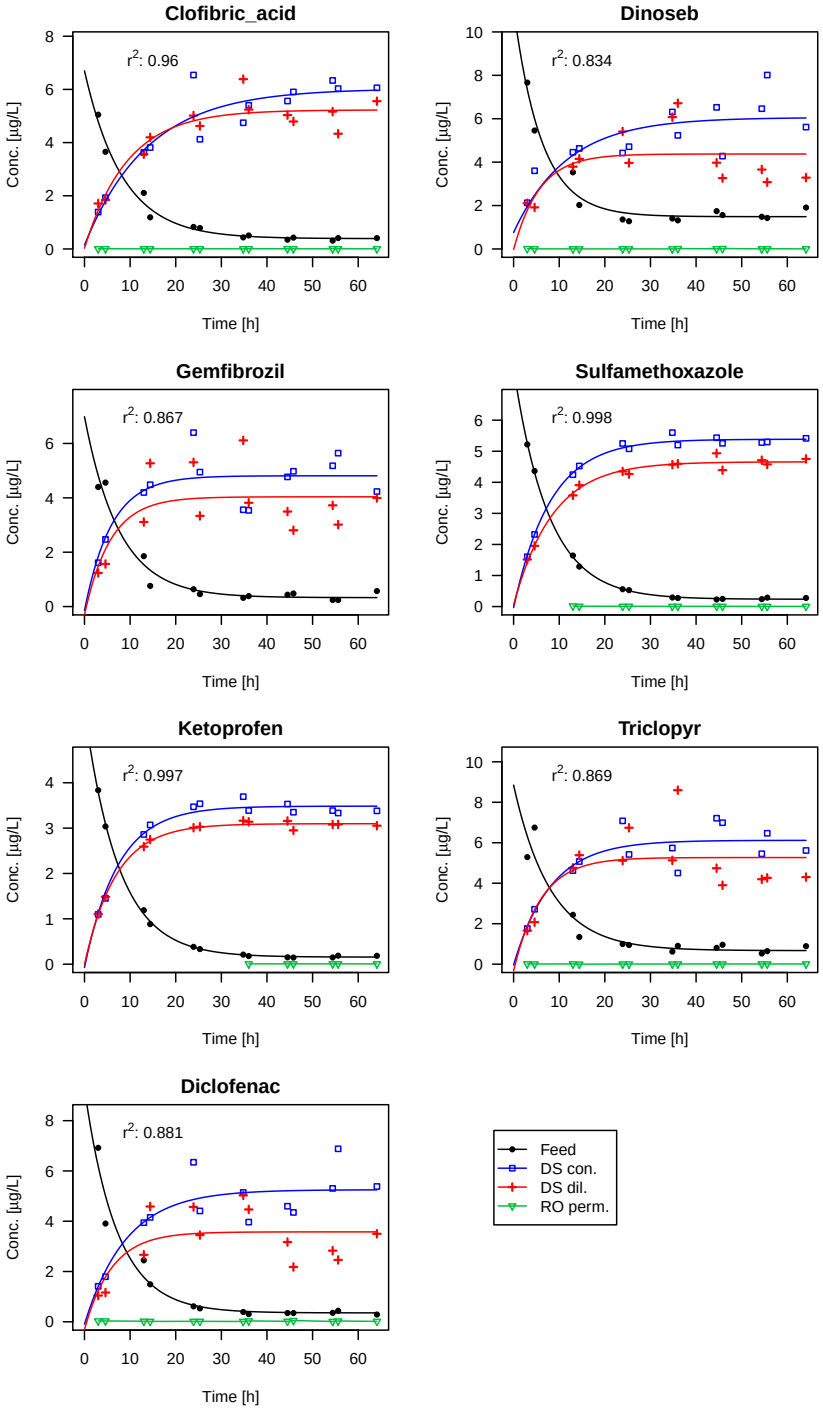

Figure 1: NaCl DS, figure 1

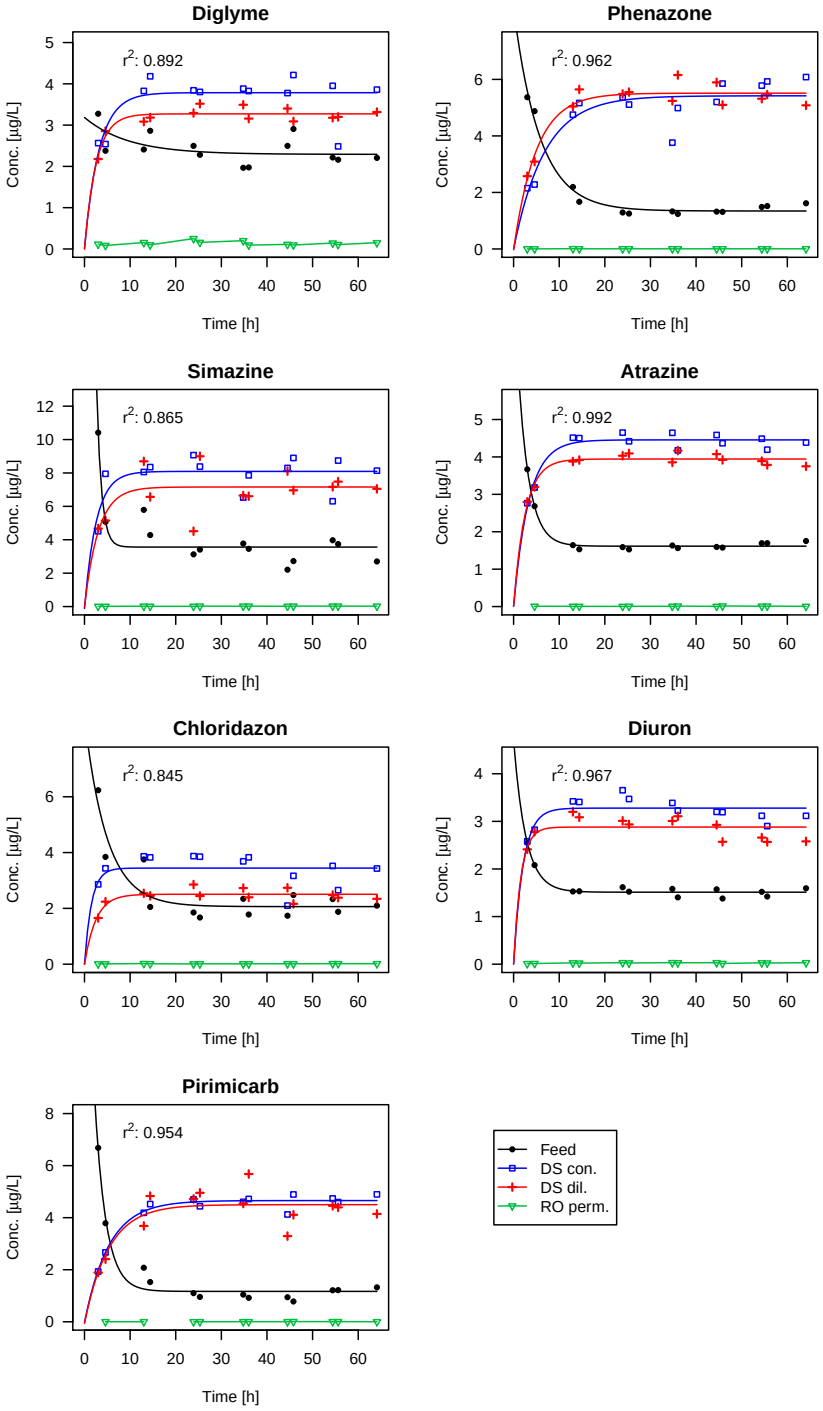

Figure 2: NaCl DS, figure 2

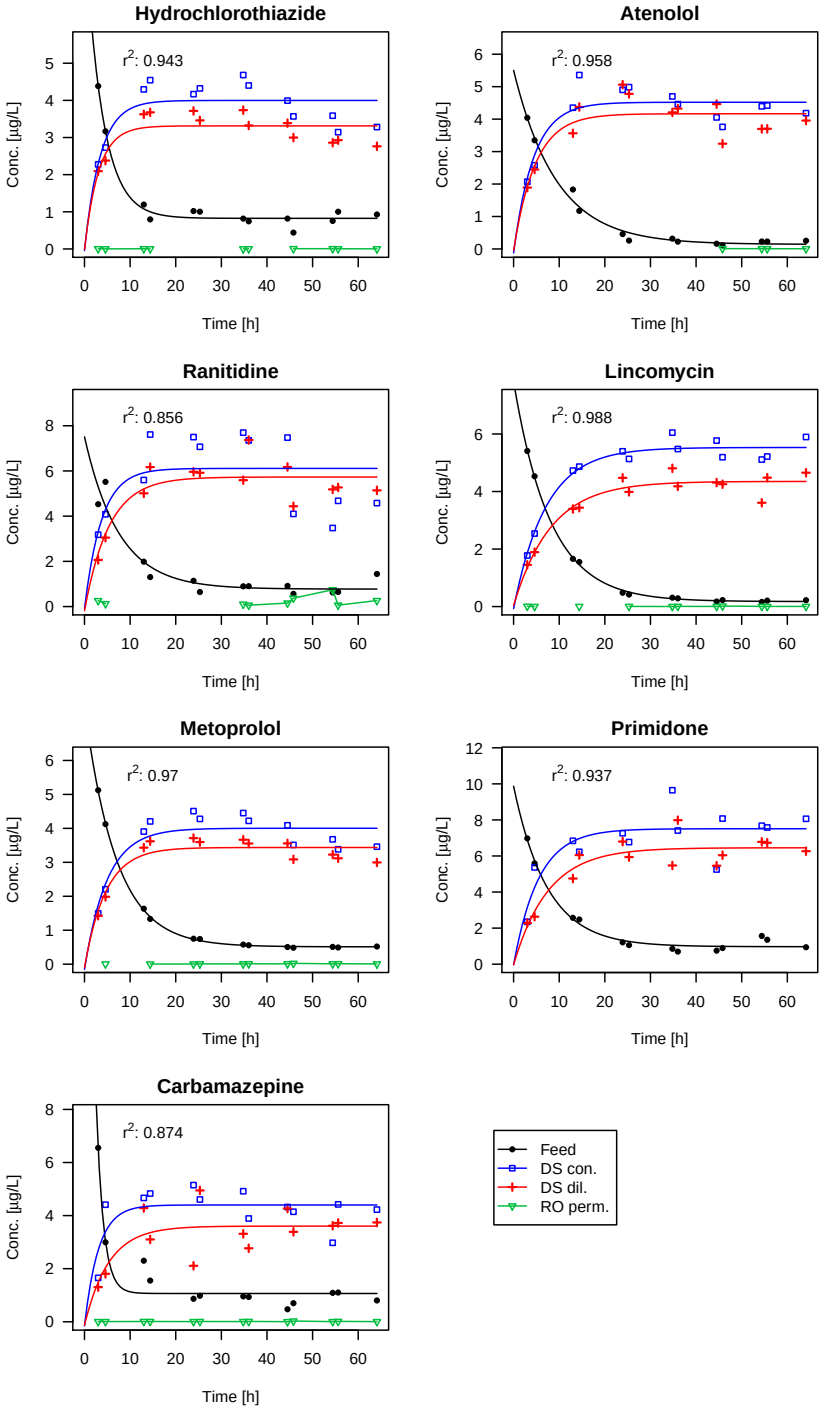

Figure 3: NaCl DS, figure 3

4. OMP concentrations during $MgCl_2$ DS experiment

Below are the OMP concentrations in the FO feed, diluted and concentrated draw solution and RO permeate obtained using $MgCl_2$ as draw solute. Solid lines are fits of Eq. 11, in all cases except RO permeate where points are joined by straight line segments. Where the RO permeate data is missing in a plot indicates that said OMP was not detected in the RO permeate.

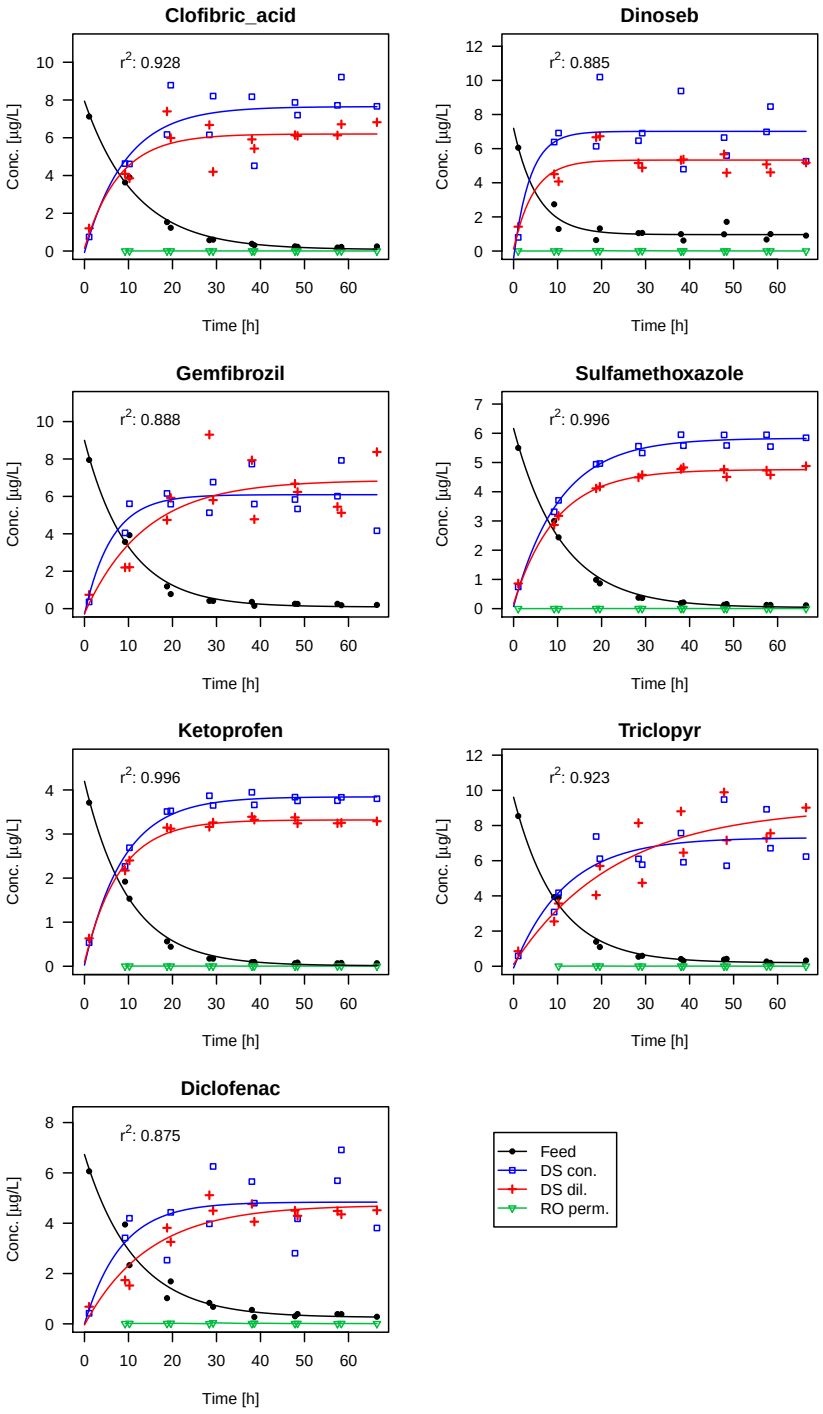

Figure 4: $MgCl_2$ DS, figure 1

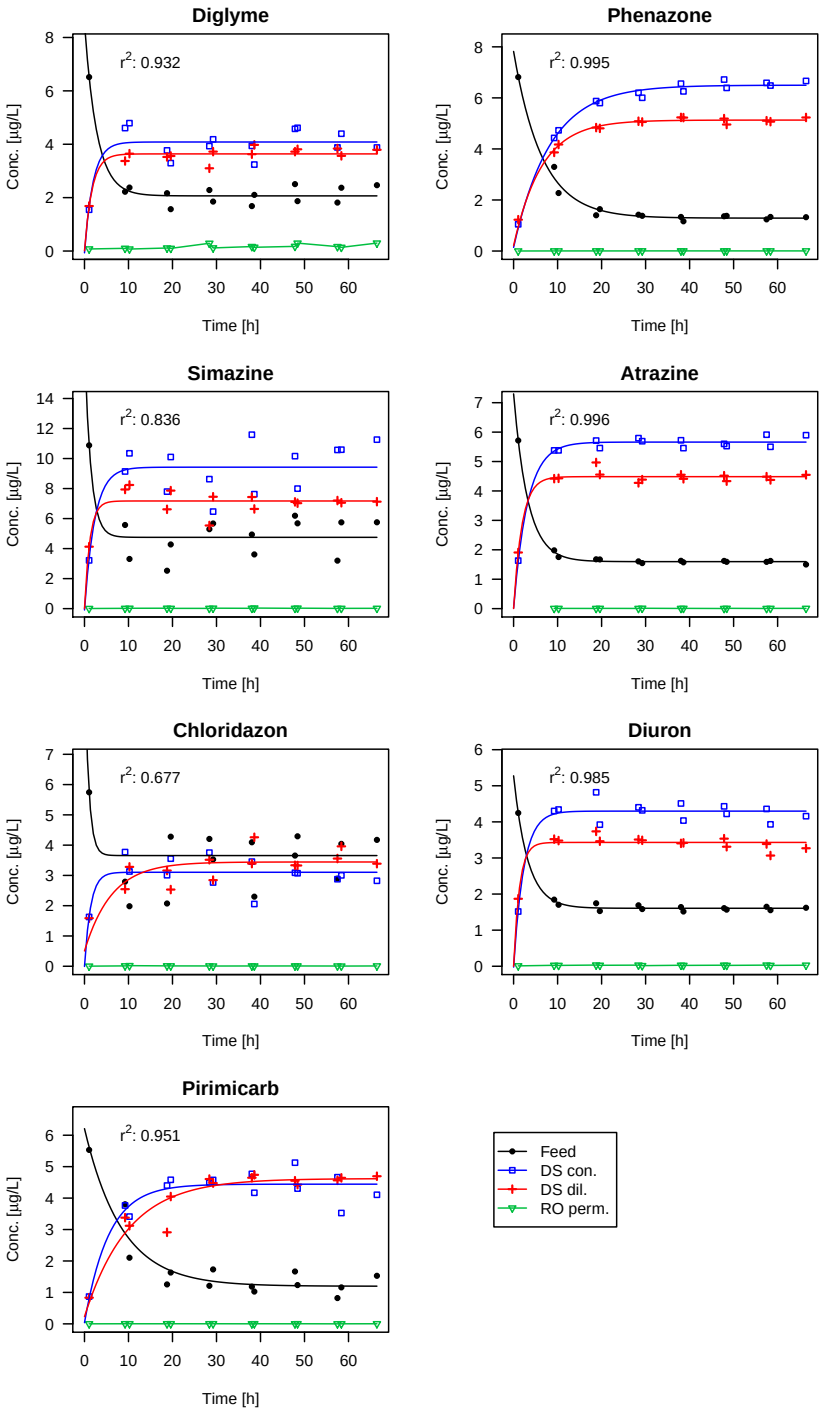

Figure 5: $MgCl_2$ DS, figure 2

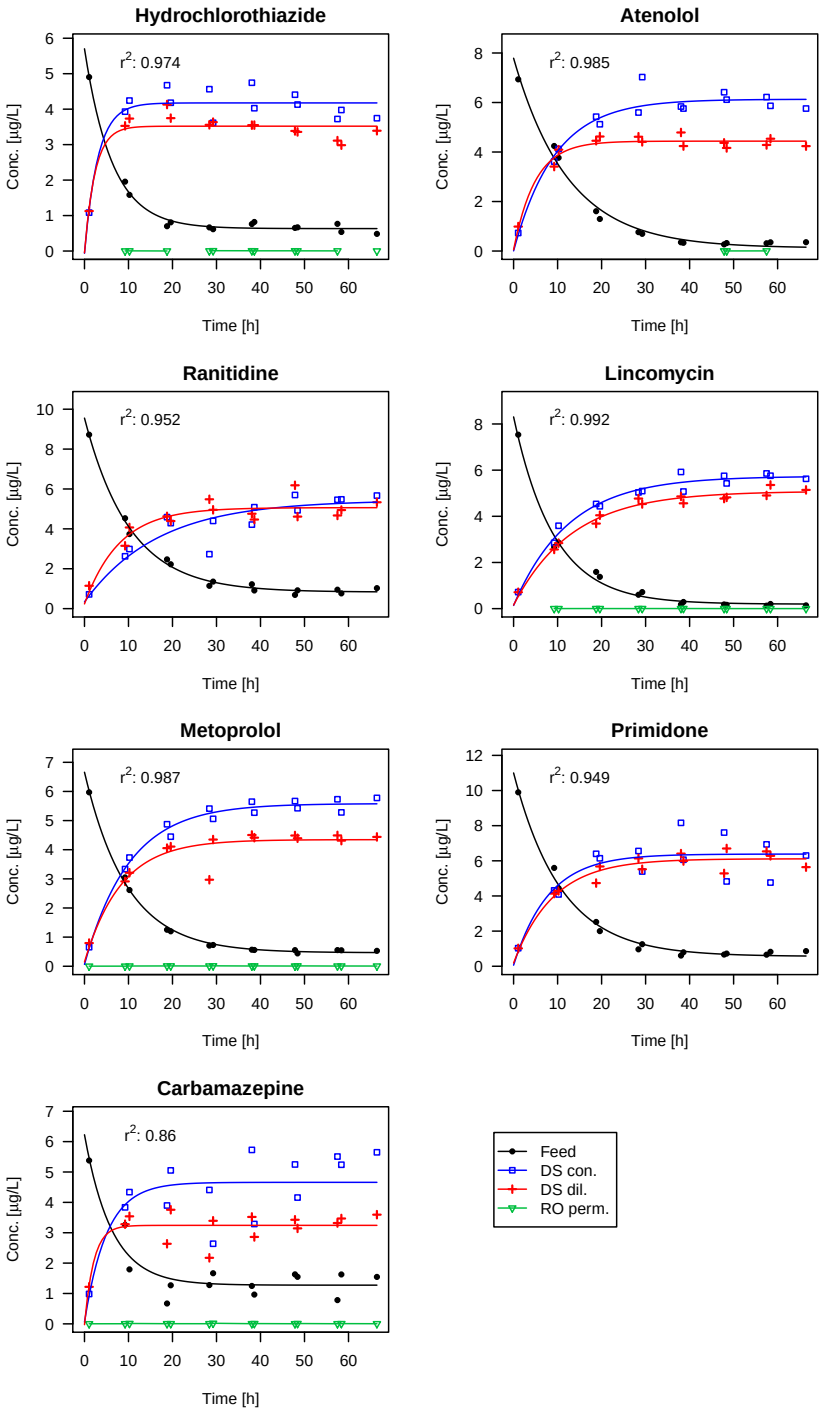

Figure 6: $MgCl_2$ DS, figure 3

5. References