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TRACE ORGANIC COMPOUNDS BROUGHT IN BY THE LAND APPLICATION OF WASTEWATER TREATMENT PLANT SLUDGES

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ABSTRACT

The behaviour of three characteristic groups of trace organic compounds (Phtalates, Nonyl Phenol Ethoxylates and Chlorophenols) in a ground-plant system has been carried out. With the aim of reclaiming biosolids for agriculture, the transfer potential has been studied in hydroponically growing tomato plants (*Lycopersicon esculentum* var. Rondello), where transfer should be optimal. Plant containers inside a temperature and humidity controlled plant house were used.

There were two types of experiment. Trace organic compounds have initially been introduced as pure substances. A second experiment has been carried out under the same conditions, but using wastewater treatment plant biosolids.

The results clearly show a difference in behaviour of the trace organic compounds according to the part of the plant and method of introduction. Generally speaking, for the experiments using pure substances, the roots absorb higher quantities of trace organic compounds and block to a greater or lesser extent their transfer to the above ground parts of the tomato plant. However, with the biosolids filtrate, the Di-ethylhexyl phtalate and the Nonyl ethoxylate phenol can be traced all over the plant.

KEYWORDS

Wastewater treatment plant biosolids, Trace Organic Compounds (Phtalates, Nonyl Ethoxylate Phenols, Chlorophenols), tomato, hydroponics, transfer.

INTRODUCTION

Trace Organic Compounds (TOC) which are found in water and/or food, are posing problems at the moment. This is because some of them have been singled out by many workers as having a disruptive effect on the endocrine system which could lead to hormonal imbalances. Consequently, all enriching agents that could be applied to the soil have to be controlled.

In France, the annual production of biosolids from wastewater treatment plants is 900 000 tonnes dry matter and 60% of this is agriculturally recycled. These biosolids make good fertilisers but may contain unwanted components. New European legislation is currently under examination to fix in particular, the level of certain TOC's : Polycyclic Aromatic hydrocarbons (PAH), Poly Chloro Biphenyls (PCB), AOX, Phtalates, Nonyl Ethoxylate Phenol (NEP), Linear Alkylbenzene Sulfonates (LAS), Dioxins and the Furanes (Ademe, 1996).

It would appear essential, in the interests of public health, to study the transfer potential into plants of these TOC's (Diercxsens et al, 1997).

To this end, an initial experiment has been carried out using pure substances and a second one with biosolids. The plants are grown hydroponically which in theory gives optimal transfer (Morard, 1995). The TOC's chosen for this study are thus ones which are highly water soluble : Phtalates, Nonyl Phenols Ethoxylates and chlorophenols. The results obtained are expressed as percentage movement of the particular TOC's into the plant

METHODOLOGY

Material

The experiment was conducted on tomato plants (*Lycopersicon esculentum cv.*), Rondello variety (de Ruiter seeds). This particular variety is a hybrid often used for experiments because of its high rate of germination (99%) and genetic homogeneity.

The containers used were 10 L galvanised buckets to avoid problems associated with PVC (presence of phtalates).

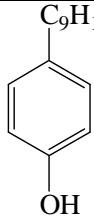
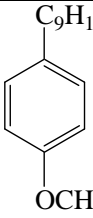
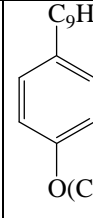
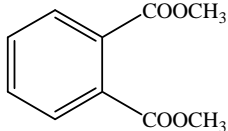
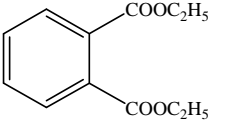
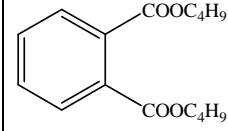
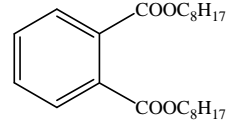
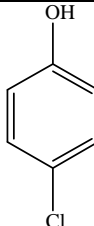
Tomato plants were grown hydroponically on aerated, non-circulating nutrient solution. This was prepared using pure salts and deionised water. It contained macronutrients (7 mmol/L of K^+ , 5 mmol/L of Ca^{2+} , 1,5 mmol/L of Mg^{2+} , 15 mmol/L of NO_3^- , 2 mmol/L of $H_2PO_4^-$ and 1,5 mmol/L of SO_4^{2-}) and micronutrients (15 mg/L of Fe, 0,49 mg/L of Mn, 0,06 mg/L of Cu, 0,11 mg/L of Zn, 0,26 mg/L of B and 0,01 mg/L of Mo). The amounts of macronutrients were calculated according to the mineral needs of the plants for the duration of the experiment. The nutrient solution was replaced twice a week. Its conductivity was 2 mS.cm⁻¹ and the pH varied from 5.2 for fresh solution to 6.5 for spent solution.

Plant house conditions : The temperature was 24°C day and 19°C night, the relative humidity was about 50% and the photo/scoto period was 14h day/10h night.

For the study of TOC transfer when introduced in the pure form (cf. Table 1), the pure substances chosen were :

- Nonyl Ethoxylate Phenols (NEP) comprising the following compounds : nonylphenol (NP), nonylphenol mono-ethoxylate (NP1EO) and nonylphenol di-ethoxylate (NP2EO).
- The phtalates in the form of four phtalate esters : dimethylphtalate (DMP), diethylphtalate (DEP), dibutylphtalate (DBP) and di-2-ethylhexyl phtalate (DEHP).
- 4-chlorophenol : used to measure the level of AOX

Table 1 – Presentation of the trace organic compounds studied

| Group of compounds | Number of compounds per group | | | |
|--------------------------------|--|---|---|--|
| Nonyl Ethoxylate Phenols (NEP) | C_9H_{19}  Nonylphenol (NP) | C_9H_{19}  Nonylphenol mono-ethoxylate (NP1EO) | C_9H_{19}  Nonylphenol diethoxylate (NP2EO) | |
| Phtalate esters |  Dimethyl phtalate (DMP) |  Diethyl phtalate (DEP) |  Dibutyl phtalate (DBP) |  Di (2-éthylhexyl) phtalate (DEHP) |
| Chlorophenols |  4-chlorophenol | | | |

For the study of TOC transfer from biosolids, the latter was taken in granular form from the drier outlet at the Toulouse wastewater treatment plant.

Experimental protocol

Experimental set-up

30 plants were used in the experiment, and Table 2 shows the plant containers which were set up. For the experiment with the pure substances, a total of 20 plants have been used :

- 8 control plants were grown in a nutrient solution to study non TOC growth
- 12 plants were grown in a TOC medium to study transfer.





For the biosolids experiments, 10 plants have been used :

- 4 controls;
- 6 growing in the biosolids filtrate.

Table 2 - Summary to show the various containers set up

| | Number of tomato plants |
|---|-------------------------|
| Pure substance experiments | |
| Controls : tomato plant + nutrient solution | 8 |
| Tomato plant + nutrient solution + NEP | 4 |
| Tomato plant + nutrient solution + phtalates | 4 |
| Tomato plant + nutrient solution + Chlorophenol | 4 |
| Biosolidss experiments | |
| Controls : tomato plant + nutrient solution | 4 |
| Tomato plant + nutrient solution + biosolids filtrate | 6 |

The pots were arranged randomly on the bench (figure 1 and 2).

Figure 1 – Diagram to show the arrangement of the pots for the pure substances experiment.
 (Key :  Control pot,  Pot containing NEP,  Pot containing the phtalates,  Pot containing the chlorophenol)

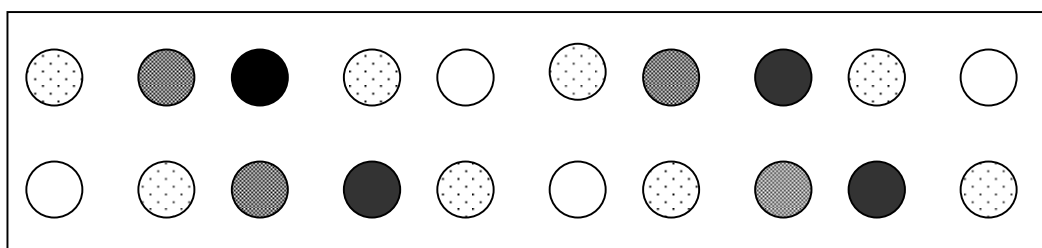


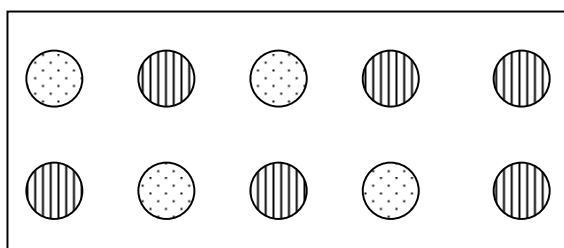


Figure 2 – Diagram to show the arrangement of the pots for the biosolids experiments.
 (Key :  Control pot,  Biosolids pot)



Quantities used

Pure substances

According to the French ministerial order of 8 January 1998, the maximum quantity authorised for land application of biosolids is 30 tonnes dry matter per ha per 10 years. For this experiment, in order to obtain clear-cut results, the quantities chosen amount to 4 times this maximum of 30 t DM/ha, added in a single dose to the plant containers.

To calculate the amounts of pure substances to be added to the containers, the limit values for TOC's in biosolids as fixed by the European directive project have been used, as has the surface area of the container.

Table 3 - Limit values for levels of trace organic compounds in biosolids (mg/kg DM) (fixed by European directive project)

| Trace organic compounds | Limit values for levels of trace organic compounds in biosolids (mg/kg DM) (fixed by European directive project) |
|--------------------------------|--|
| NEP ¹ | 50 |
| Phtalates (DEHP ²) | 100 |
| AOX ³ | 500 |

¹ Sum of the compounds : nonylphenol, nonylphenol mono-ethoxylate and nonylphenol diethoxylate

² Di (2-ethylhexyl) phtalate.

³ Sum of the adsorbable organic halogen compounds

Calculation of the NEP dose used :

$$\begin{aligned}\text{NEP limit value in biosolids} &= 50 \text{ mg/kg DM/10 yr} \\ &= 50 \text{ g/t DM/10 yr}\end{aligned}$$

$$\text{Maximum flux} = 30 \text{ t DM/ha/10 yr}$$

$$4 \times \text{maximum flux} = 120 \text{ t DM/ha/10 yr}$$

Taking the surface area of the container as 0,07 m² (average value).

$$\text{The dose used is thus : } \frac{120 \times 50 \times 0,07}{10000} = 0,042 \text{ g/container}$$

The above calculation has been used for the other TOC's, and the values obtained are given in Table 4.

Table 4 – Dose and concentration of pure substance trace organic compounds introduced into the container's initial solution

| | | Container dose (mg) | Container initial concentration ¹ (mg/L) |
|-----------|-------------------------|---------------------|---|
| NEP | Sum of (NP+NP1EO+NP2EO) | 42 | 5.25 |
| Phtalates | DMP | 84 | 10.5 |
| | DEP | 84 | 10.5 |
| | DBP | 84 | 10.5 |
| | DEHP | 84 | 10.5 |
| AOX | 4-chlorophenol | 420 | 52.5 |

¹ Each container holds 8 L of nutrient solution.

Biosolids

Preliminary experiments showed that direct introduction of the ground-up biosolids into the container lead to water stress in the plant and therefore the filtrate was used.

For quantity, the amount normally used in agriculture, i.e. 15 tonnes dry matter per hectare over 10 years, was taken. Thus 105g of ground-up biosolids granules were mixed into 1 L of demineralised water. This mixture was stirred for 24 hours in a 6 L glass beaker placed on a horizontal, rotary mechanical stirrer, and then filtered on a screening column down to 32µm in order to recuperate the biosolids filtrate.

Cultivation technique

Cultivation was in several stages and a summary is given in Figures 3 and 4

Figure 3 - Diagram to show the various cultivation stages for the experiments using pure substances

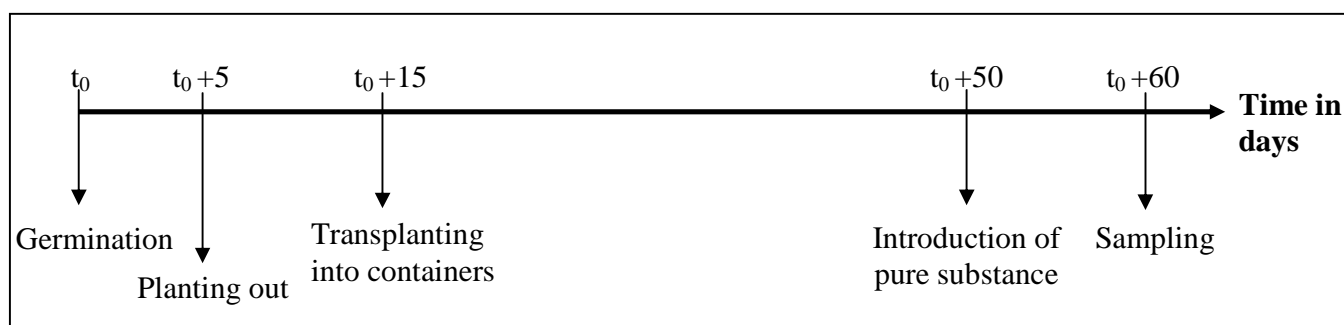
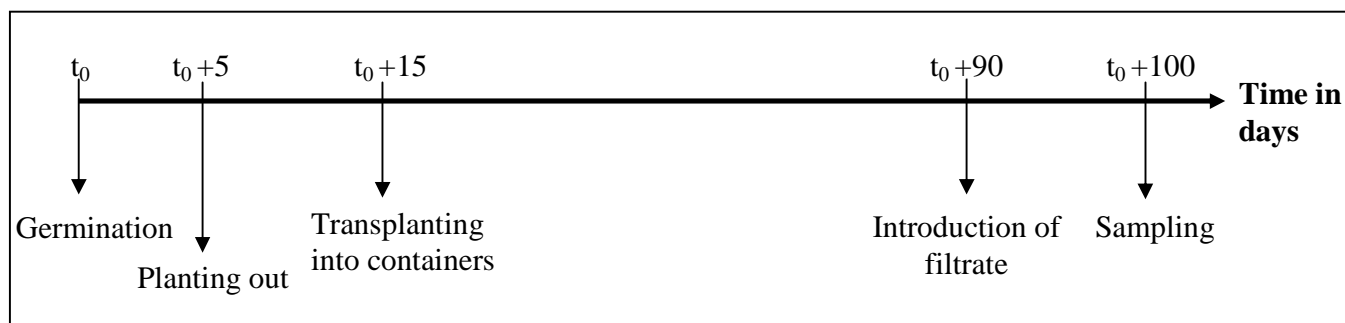
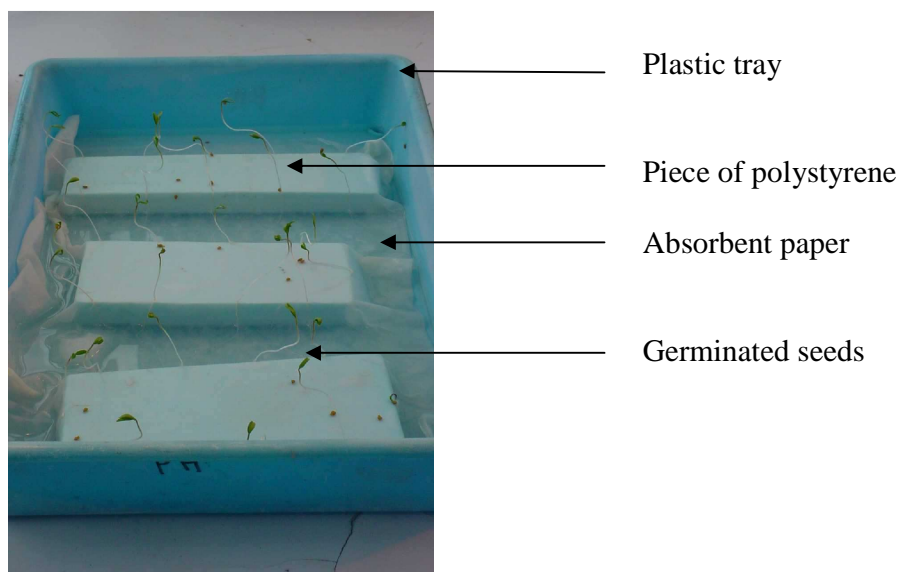


Figure 4 - Diagram to show the various cultivation stages for the experiments using biosolids



Germination : About 20 tomato seeds are germinated on pieces of polystyrene, covered with thick absorbent paper dipping into a plastic tray such that the seeds are in contact with the water in the tray bottom. The tray is than placed in a dark, germination cupboard for 3 days. The germinating seeds in the tray are then put into a phytotron for 2 days. This is an enclosure lit by sodium lamps where there are controlled conditions of light, humidity and temperature : 14 hours light per 24 hours, 50% humidity in the air and a temperature of $24 \pm 1^\circ\text{C}$ by day and $18 \pm 1^\circ\text{C}$ by night.

Figure 5 – View of a trough after germination



The plants then continue their development in a plant house where conditions are controlled as a function of the external temperature and light. Blinds, ventilation and lighting ensure optimum conditions (average temperature 24°C , 14 hours light). The 10 cm long seedlings are transferred into troughs containing 20 litres of nutrient solution. They are wrapped in cotton wool and inserted into special holes in the trough covers, with just the root dipping into the solution (figure 6 and 7). A bubbler is put into the solution to oxygenate it, with an on/off cycle of 6 minutes and 12 minutes respectively.

Figure 6 – View of a trough after planting out

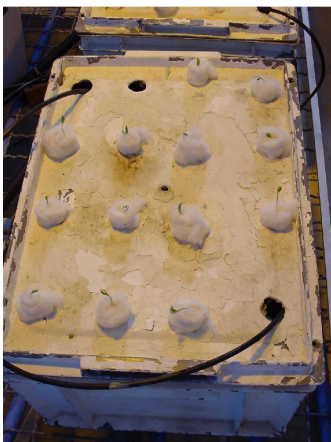


Figure 7 – Detailed shot to show roots



Once the plants have attained a height of 10 cm, they are transplanted individually into the galvanized containers holding 8 litres of nutrient solution, each oxygenated with an individual bubbler. This solution is topped up with demineralised water to compensate for losses through transpiration and evaporation. Once the solution conductivity falls below half that of its original value, it is renewed.

The pure substances or biosolids filtrate are introduced into these containers after 50 and 90 days growth respectively.

Ten days after the introduction of the pure substances or the biosolids filtrates, the plants are sampled in order to study the fruits, the leaves, the sap and the roots. The main stem of each plant is cut about 5 cm above the container cover and the fruits and leaves are removed (Figure 8). A 10 cm long silicone tube is fitted over the cut stem stump to collect the sap, which comes up bit by bit into it. This system has been improved by putting a syringe at the other end of the tube to mimic the natural transpiration tension in the plant (Figure 10). Between 50 and 100 mL of sap has been collected for all the plants. Once this is finished, the roots in contact with the nutrient solution are rinsed in demineralised water and weighed (Figure 9). All samples are put in aluminium foil trays into a freezer at -25°C .

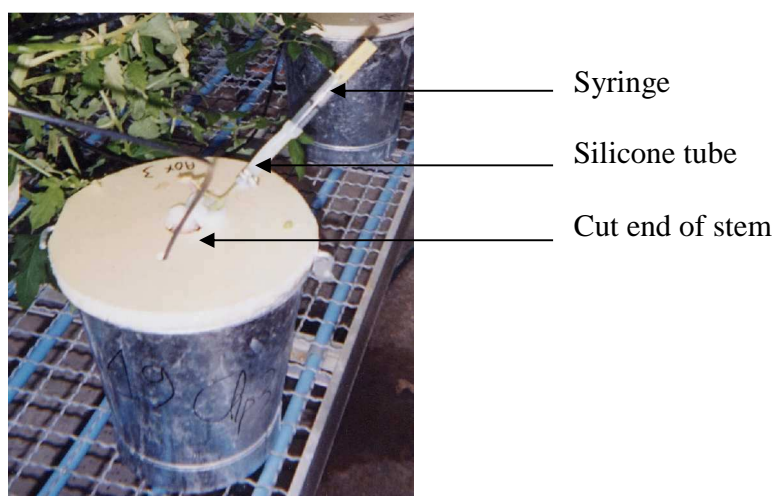
Figure 8 – Fruits before sampling



Figure 9 – Roots before sampling



Figure 10 – Collecting the sap



Analytical Methods

Pre-treatment

The samples were first completely homogenized using a household blender. From the homogenate, a 10g wet sample is weighed into a 40 mL vial with a Teflon-lined screw cap.

Determination of chlorophenols

10 mL methanol is added to the sample. The vial is closed and placed in an ultrasonic bath for 15 min. Then it is shaken on a shaker for 30 min and the solid material allowed to settle overnight. From the supernatant, 1 mL is transferred to a 20 mL headspace vial. 10 mL pure water (bottled drinking water) is added, followed by 0.5 g potassium carbonate and 500 μ L acetic anhydride. The vial is closed and analysed by SPME-GC-MS. Solid phase micro-extraction is performed in the headspace using a 100 μ m PDMS fiber. The extraction time is 15 min and extraction temperature 50°C.

After extraction, the PDMS fibre is thermally desorbed in a split/splitless inlet. The analyses were performed on an Agilent 6890 GC - 5973 MSD system.

The phenols are analysed as acetates under the following conditions:

Column: 30 m x 0.25 mm i.d. x 0.25 μ m HP-5MS.

Injection: splitless, 250°C, 1 min purge time.

Carrier: 53 kPa constant pressure

Oven Temperature: 70°C – 1 min – 5°C/min – 220°C – 25°C/ min – 280°C.

The MS is operated in SIM mode. Calibration is versus an external standard (water sample spiked with chlorophenols and analysed by SPME-GC-MS under the same conditions).

Determination of phthalates

Prior to use, the vials are rinsed with pure cyclohexane. The cyclohexane was tested in our lab and traces of phthalates were below 2 ppb (2 µg/L).

To the sample, 10 mL methanol is added plus 10 µL of a 100 ng/µL internal standard solution (d4-DEHP), (IS amount = 1000 ng). The vial is closed and placed in an ultrasonic bath for 15 min.

The vials are opened and 10 mL cyclohexane is added and the ultrasonic extraction is repeated for another 15 min.

Next, 10 mL water is added. We use Vittel or another bottled drinking water, as this gives lower blank values for phthalates than HPLC grade, distilled laboratory water or MilliQ water. The vial is shaken on a shaker for 30 min.

Finally the layers (cyclohexane= upper layer, water/methanol = bottom layer) are allowed to separate and approximately 1 mL of the clear supernatant is transferred into an autosampler vial. The theoretical concentration of the internal standard in the injection solution is thus 1000 ng/10mL or 100 pg/µL.

The analyses are performed on an Agilent 6890 GC - 5973 MSD system.

The analytical conditions used for GC-MS are as follows :

Column: 30 m x 0.25 mm i.d. x 0.25 µm HP-5MS.

Injection: 1 µL, splitless, 280°C, 0.75 min purge time.

Carrier: 1 mL/min helium (constant flow, 53 kPa at 50°C).

Oven Temperature: 50°C – 1 min – 20°C/min – 310°C – 6 min.

Detection: MS in SIM mode (ions: 149, 153, 163, 279, 293 and 307)

Determination of nonylphenols

To the sample, 10 mL methanol is added plus 10 µL of a 100 ng/µL internal standard solution (4-tert.octylphenol), (IS amount = 1000 ng). The vial is closed and placed in an ultrasonic bath for 15 min. The vials are opened and 10 mL diethylether is added and the ultrasonic extraction is repeated for another 15 min.

Next, 20 mL of a saturated sodium chloride solution in water is added and the vial is shaken on a shaker for 30 min.

The mixture of organic solvents and water is filtered through a paper filter into a 100 mL separating funnel. The filter (with plant material) is rinsed with another 10 mL diethylether and another 20 mL sodium chloride is added to the funnel. The separating funnel is shaken and the phases are allowed to separate. The diethylether layer is isolated, dried over sodium sulphate and concentrated under nitrogen using a Zymark Turbovap system. Prior to evaporation, 1 mL iso-octane is added and the sample is concentrated to 1 mL. The theoretical concentration of the internal standard in the injection solution is thus 1000 ng/1mL or 1 ng/µL.

The analyses were performed on an Agilent 6890 GC - 5973 MSD system.

The analytical conditions used for GC-MS are as follows :

Column: 30 m x 0.25 mm i.d. x 0.25 µm HP-5MS.

Injection: 1 µL, splitless, 280°C, 0.75 min purge time.

Carrier: 1 mL/min helium (constant flow, 53 kPa at 50°C).

Oven Temperature: 50°C – 1 min – 20°C/min – 320°C – 5 min.

Detection: MS in SIM mode (ions: 135, 206, 220)

The internal standard can be monitored on ion 135 with ion 206 as confirmation ion. Nonylphenol can be monitored on ion 135 as well, with ion 220 as confirmation ion. The internal standard is a pure

compound resulting in a single peak (retention time 9.1 min). Nonylphenol elutes as a complex mixture of isomers between 9.6 and 10.1 min. The extracted ion chromatogram at ion m/e 135 is manually integrated as area sum from 9.6 to 10.1 min.

RESULTS

Base state : Levels of TOC's in wastewater treatment plant biosolids

The levels of TOC's in the biosolids have been determined : cf. Table 5.

Similarly, the levels of TOC's in the biosolids filtrate have been determined ; cf. Table 6

Table 5 – Levels of trace organic compounds in the biosolids in mg/kg DM

| | Levels of trace organic compounds in the biosolids (mg/kg DM) |
|------|---|
| NEP | 93 |
| DEHP | 165 |
| AOX | 200 |

Table 6 – Levels of trace organic compounds in the biosolids filtrate, in µg/L

| | Levels of trace organic compounds in the biosolids filtrate (µg/L) |
|----------------|--|
| NEP | 76 |
| DEHP | 2680 |
| DEP, DMP, DBP | < 40 |
| 4-chlorophénol | < 40 |

Plant matter produced

The different fresh plant matter masses are shown in figures 11 and 12.

Figure 11 – Average production of fresh matter per container in the pure substance experiments

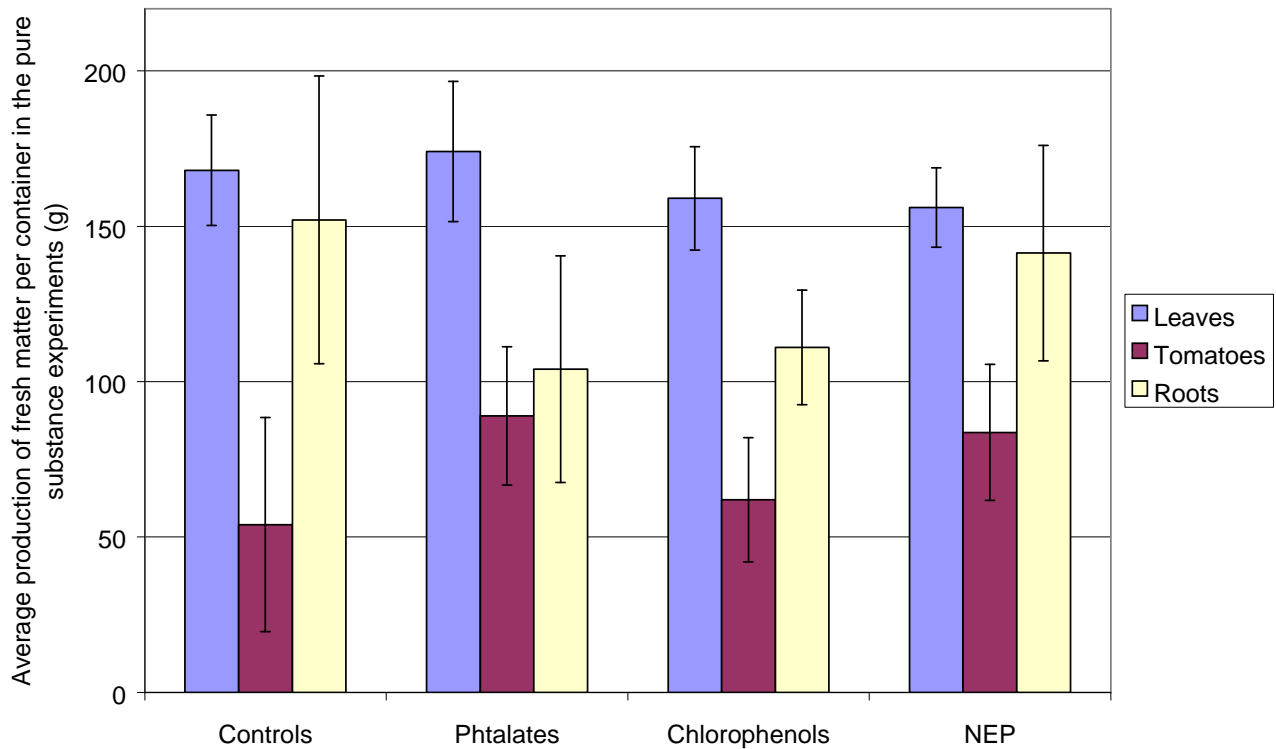
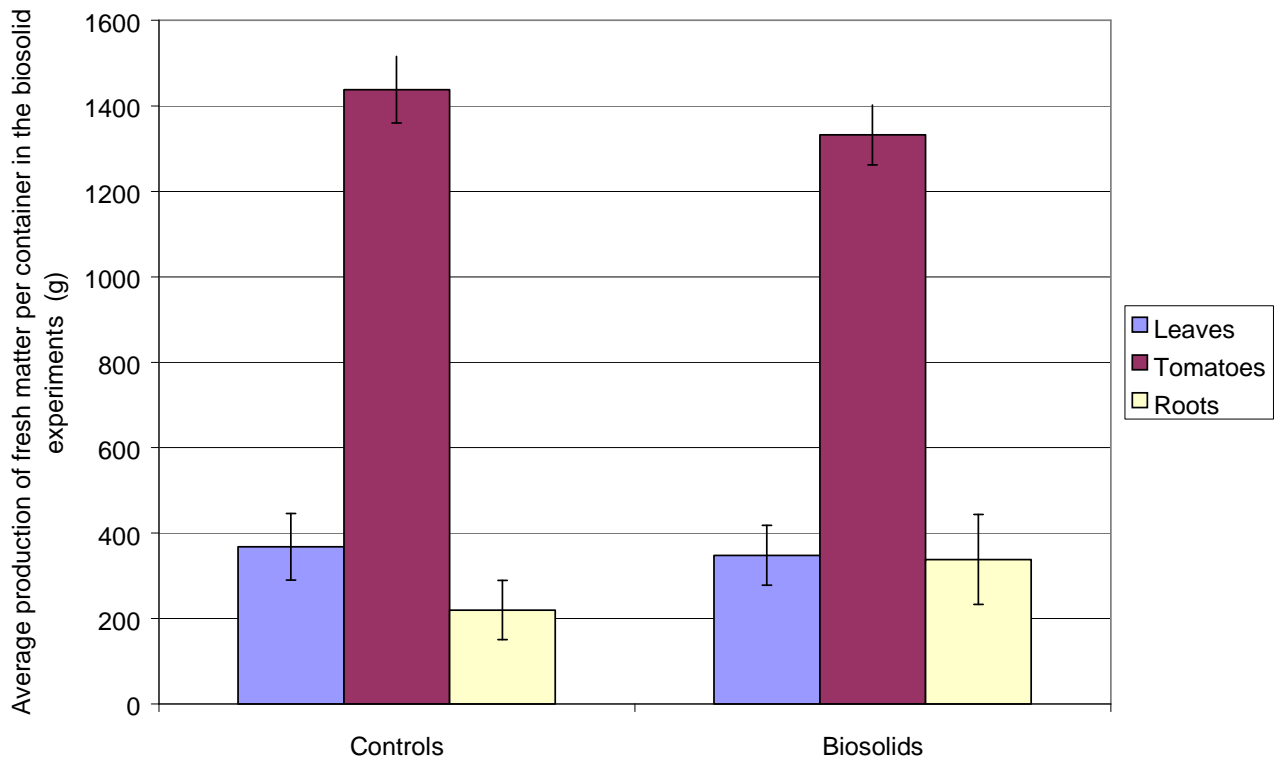


Figure 12 – Average production of fresh matter per container in the biosolids experiments



Transfer of trace organic compounds in the tomato plant

Tables 7 and 8 show the average levels of Phtalates, Nonyl Ethoxylate Phenols and Chlorophenol found in the roots, sap, leaves and fruits of tomato plants grown in nutrient solutions with additional pure trace organic compounds or biosolids filtrate. The control plants have been used as blank values for the analyses.

Table 7 – Results of the phtalate analyses

| Sample | Level of DMP ¹ | | Level of DEP ² | | Level of DBP ³ | | Level of DEHP ⁴ | |
|-----------------------------------|---------------------------|----------------------|---------------------------|----------------------|---------------------------|----------------------|----------------------------|----------------------|
| | ng/g FM ⁵ | ng/g DM ⁶ | ng/g FM ⁵ | ng/g DM ⁶ | ng/g FM ⁵ | ng/g DM ⁶ | ng/g FM ⁵ | ng/g DM ⁶ |
| Pure substance experiments | | | | | | | | |
| Roots | <10 | <100 | <10 | <100 | 59 | 617 | 10450 | 132912 |
| Sap | <10 | nm ⁷ | 14 | nm ⁷ | <10 | nm ⁷ | <10 | nm ⁷ |
| Leaves | <10 | <50 | 378 | 2368 | <10 | <50 | 39 | 244 |
| Tomatoes | <10 | <100 | <10 | <100 | <10 | <100 | <10 | <100 |
| Biosolids experiments | | | | | | | | |
| Roots | <10 | <100 | <10 | <100 | <10 | <100 | 118 | 1350 |
| Sap | <10 | nm ⁷ | <10 | nm ⁷ | <10 | nm ⁷ | 314 | nm ⁷ |
| Leaves | <10 | <50 | <10 | <50 | <10 | <50 | 37 | 234 |
| Tomatoes | <10 | <100 | <10 | <100 | <10 | <100 | <10 | <100 |

¹ DMP : dimethylphtalate,

² DEP : diethylphtalate,

³ DBP : dibutylphtalate,

⁴ DEHP : Di (2-éthylhexyl)phtalate,

⁵ FM : Fresh matter,

⁶ DM : Dry matter,

⁷ nm : not measurable

Table 8 – Results of the Nonyl Phenols Ethoxylates and Chlorophenol analyses

| Sample | Amount of NEP ¹ | | Amount of 4-chlorophenol | |
|-----------------------------------|----------------------------|----------------------|--------------------------|-----------------|
| | ng/g FM ² | ng/g DM ³ | ng/g FM | ng/g DM |
| Pure substance experiments | | | | |
| Roots | 372 | 4262 | 36769 | 421262 |
| Sap | 53 | nm ⁴ | 91 | nm ⁴ |
| Leaves | 64 | 408 | 429 | 2735 |
| Tomatoes | <10 | <100 | <10 | <100 |
| Biosolids experiments | | | | |
| Roots | 271 | 3114 | 23 | 263 |
| Saps | 29 | nm ⁴ | <10 | nm ⁴ |
| Leaves | 131 | 818 | <10 | <50 |
| Tomatoes | 86 | 1615 | <10 | <100 |

¹ NEP : Nonyl ethoxylate phenols,

² MF : Fresh matter,

³ MS : Dry matter,

⁴ nm : not measurable.

DISCUSSION

Base state : Levels of trace organics in the wastewater treatment plant biosolids

Calculation of the theoretical concentration of NEP introduced by the biosolids filtrate :

Amount of NEP in the biosolids = 93 mg/kg DM

Common/good agricultural practice recommends a flux of : 15 t DM/ha/10 yr

Taking the surface area of the container as 0,07 m² (average value).

The theoretical concentration of NEP is thus : $\frac{93 \times 15000 \times 0,07}{10000} = 9,8$ mg/container

And the container holds 8 L of nutrient solution

Hence, the theoretical concentration of NEP introduced by the biosolids filtrate in the container is 1,22 mg/L.

But, the actual level of NEP in the biosolids filtrate has also been determined (cf. Table 6). Thus the true concentration in the container is calculated by taking into account that there is one volume of filtrate for 7 volumes of nutrient solution in each container (cf. Table 9).

The transfer coefficient is defined as :

$$\frac{\text{True concentration of trace organics in container}}{\text{Theoretical concentration of trace organics brought in to container by biosolid}} \times 100$$

This same calculation has been carried out for the other TOC's and the values obtained are given in Table 9.

Table 9 – Comparison of the theoretical amounts of trace organic compounds

| | Theoretical concentration of trace organic compounds in the container (mg/L) | True concentration of trace organic compounds in the container (µg/L) | Transfer coefficient (% which passes) |
|----------------------|--|---|---------------------------------------|
| NEP | 1,22 | 9,5 | 6,3 |
| DEHP | 2,16 | 335 | 15,5 |
| DEP, DMP, DBP | - | < 5 | - |
| AOX (4-chlorophénol) | 26,25 | < 5 | 0,19 |

The table shows that not all the trace organic compounds present in the biosolids are found in the filtrate. However, the fractions which are present in the filtrate are also those which are most available for transfer into the plant

Plant matter produced

It can be seen (cf. Figures 11 and 12) that there is a difference between the average mass of the tomato plants in the pure substance experiments and those in the biosolids ones. This can be explained by the

plant's stage of development. Sampling for the pure substance experiments was undertaken when the 3rd cluster of flowers had developed (after 60 days) whereas for the biosolids experiments sampling has been possible at the 5th cluster stage (100 days).

We have calculate the ratio (R) between :

$$\frac{\text{average production of fresh matter per container in pure substance experiments or filtrat experiments (g)}}{\text{average production of fresh matter per container in control (g)}}$$

Table 10 – Comparison with ratio of mass production in each experiments

| | R | | | R |
|----------|-----------|--------------|-----|---------|
| | Phtalates | Chlorophenol | NEP | Filtrat |
| Leaves | 1,0 | 0,9 | 0,9 | 0,9 |
| Tomatoes | 1,6 | 1,1 | 1,5 | 0,9 |
| Roots | 0,7 | 0,7 | 0,9 | 1,5 |

For the pure substance experiments, the ratio between the average mass of the control plants and the average masses produced after introduction of the pure substances is quite the same and significantly equal to one. And the same is true for the biosolids experiments. It is thus interesting to note that the growth of the plant is not disturbed by the introduction of pure substances or biosolids filtrates.

Transfer of trace organic compounds in the tomato plant

Phtalates

An analysis of the results in Table 7 show that for the experiment using pure substances, the level of DMP is always below the detection threshold of the apparatus. The DEP is present in the leaves and the DBP in negligible quantities in the roots. Only the DEHP is present in large quantities in the roots. In fact, DEHP is known to have a high affinity for organic matter (Gron et al, 2000). Furthermore, this result agrees with those of Diercxsens and Tarradellas (1983) and Diercxsens et al (1987) who found the highest concentrations of phtalates in the roots of their plants

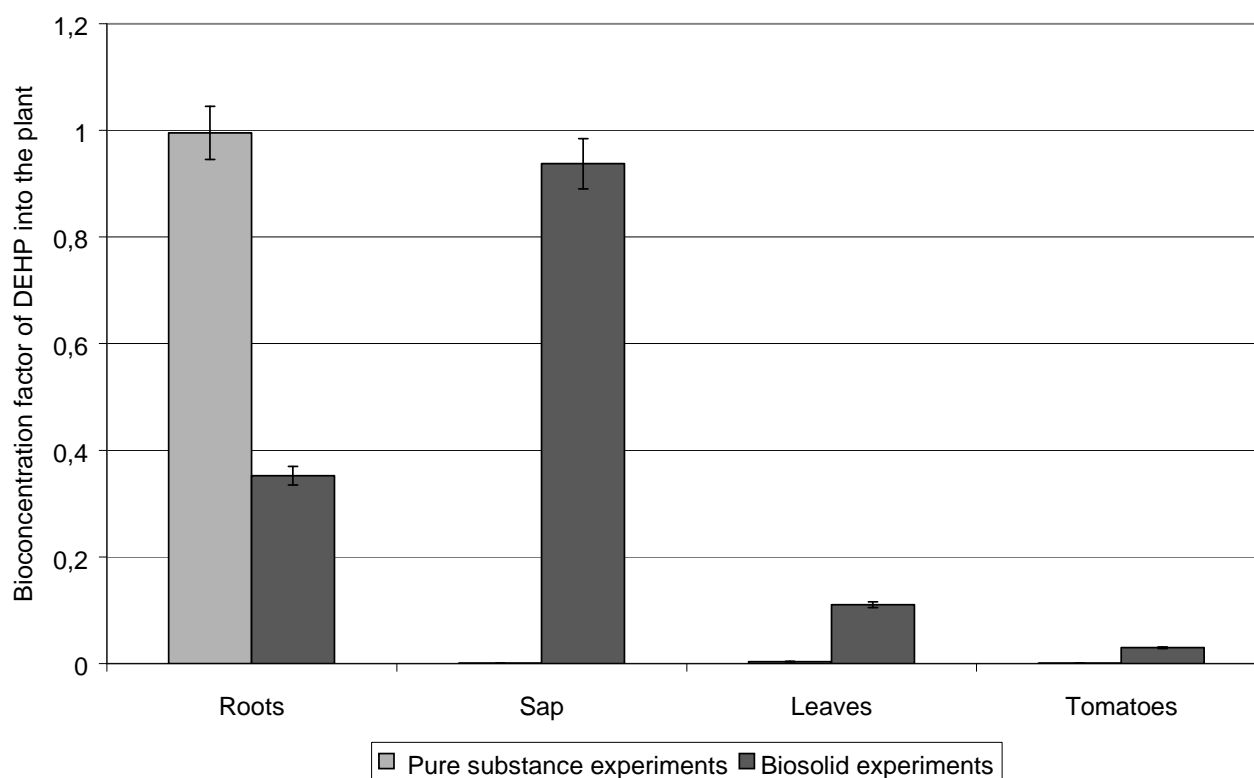
In the biosolids experiments, the levels of DMP, DEP and DBP in all parts of the plant are all below the detection threshold of the apparatus, and this can be explained by the fact that their initial concentration in the biosolids filtrate is very low. However, the DEHP is found in the roots, leaves and sap. Studies by Kirchmann and Tengsved (1991), Herring et al (1988) and Shea et al (1982) have also produced evidence showing its transfer to the plant.

These results show that as far as phtalate transfer is concerned, the general rule, should be to prioritize DEHP.

However, to compare the two experiments, it is important to study the percentage movement of TOC's into the plant, and these results are expressed in terms of a plant bioconcentration factor (cf. Figure 13). This is defined as :

$$\text{Bioconcentration factor} = \frac{\text{Concentration of DEHP in a part of the plant}}{\text{Initial concentration in the container}}$$

Figure 13 – Comparison of the pure substance and biosolids experiments in terms of movement of the DEHP into the tomato plant



The comparison shows a difference in the behaviour of DEHP. When this is in the pure form it is blocked by the roots. However in the biosolids form it can be traced all the way up the plant to the fruit, and this difference can be explained by the presence of other tensioactive compounds in the biosolids, favouring the uptake of the DEHP by the plant's roots.

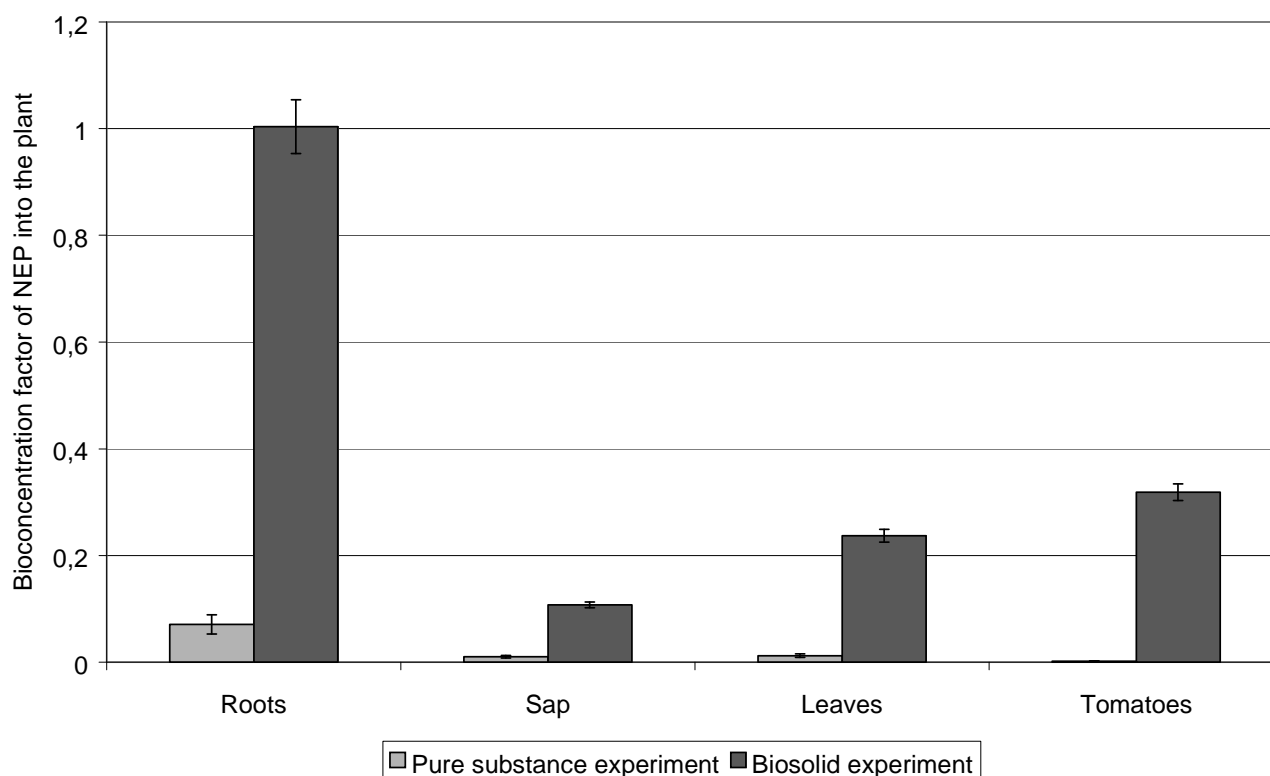
Nonyl Ethoxylate Phenols

The results (cf. Table 7) show that for the pure substance experiments the NEP's are present in large quantities in the roots and in smaller quantities in the sap and the leaves. In the biosolids experiments they are found in all parts of the plant and even in the fruit.

In the same way, we have expressed these results in terms of a plant bioconcentration factor defined as :

$$\text{Bioconcentration factor} = \frac{\text{Concentration of NEP in a part of the plant}}{\text{Initial concentration in the container}}$$

Figure 14 – Comparison of the pure substance and biosolids experiments in terms of movement of the NEP into the tomato plant



Comparing the two experiments shows that the NEP's are behaving differently. It can be seen that the biosolids filtrate facilitates the absorption of NEP by the plant.

4-chlorophenol

It can be clearly seen that although the 4-chlorophenol appears to move easily into the roots, there does not seem to be any subsequent movement to the other parts of the plant.

However, the actual biosolids filtrate matter poses analytical problems concerning detection limits. The detection threshold achieved so far is still not satisfactory. For the plant material on the other hand, the detection limit achieved is 10 ng/g of fresh matter. Therefore it is not yet possible to compare the results for the pure substances and biosolids experiments in terms of bioconcentration factor in the plant, for this compound.

CONCLUSIONS

This paper deals with a study of the transfer of trace organic compounds in containers of plants with the aim of agronomic recycling of biosolids. To this end, the bioavailability of phthalates, nonyl ethoxylate phenols and chlorophenols has been studied in hydroponic culture using two types of experiments. Firstly, tomato plants have been grown in containers where the trace organic compounds have been

introduced directly in the form of the pure substances. A second experiment has been carried out under the same growth conditions using wastewater treatment plant biosolids. The transfer of the trace organic compounds has been followed in the various parts of the tomato plants.

No significant differences in growth have been observed (regardless of TOC) between the tomato plants grown in nutrient solution alone, those in nutrient solutions plus pure substances and those in nutrient solutions with biosolids filtrate

In general, for the experiments using pure substances, the roots absorb greater amounts of trace organic compounds and block to a greater or lesser extent, their transfer to the above ground parts of the plant. In the experiments with the biosolids filtrates, the DEHP and the NEP have been found and traced all over the plant.

These experiments must be concluded by a study of the flux of trace organic compounds in a liquid medium into the plant. Nevertheless, it is clear that the trace organic compounds behave in different ways in the plant according to whether they have been introduced in the form of pure substances or as part of a biosolids matrix.

Furthermore, because of the type of experiment chosen, the results obtained are theoretically optimised in terms of the transfer process. And they have to be confirmed via experiments taking place at the moment in soil, closer to real conditions, in order to evaluate the real impact of agronomic recycling of wastewater treatment plant biosolids.

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