A tool to evaluate the fertiliser value and the environmental impact of substrates from wastewater treatment

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Abstract Fertilisers may contain pollutants that are applied to the field together with the nutrients. Comparing fertilisers is difficult because of their different concentrations of nutrients and pollutants. In this study an already existing model was taken. It was further developed to compare nutrient fluxes (N, P, K, Ca, Mg, S, humus) and pollutants (heavy metals and pharmaceuticals) of pig and cattle slurry as well as human urine. The data used is taken from literature and, in the case of pharmaceuticals in urine, daily excretion rates were calculated. An amount of 19 $m^3 ha^{-1} a^{-1}$ undiluted urine can be applied, limiting factor is sulphur. Without taking over-fertilisation into account, an addition of mineral fertiliser is required to any organic fertiliser application. In general, heavy metal, antibiotic, and hormone fluxes are higher by using animal manure then urine as fertiliser. However, additional loads of other pharmaceuticals consumed by humans have to be considered. Overall, the model is a suitable tool worthwhile to be extended in aspects of hygiene, environmental impacts as for example, degradation processes as well as ecotoxicology.

Keywords Heavy metals; model; nutrients; organic fertiliser; pharmaceuticals; yellowwater

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Introduction

The process of wastewater treatment generates substrates that can be used as fertiliser in agriculture. In particular, new systems diverting urine and separating faecal matter provide products with relatively high nutrient contents. These products can be used themselves or be converted to new fertilisers for agriculture.

Fertilisation guarantees high yields in plant production. Quantity, timing, and combination of fertilisers according to actual crops and crop rotation, as well as regulating laws on fertiliser use, fertiliser type, biowaste and sewage sludge application have to be considered to reach an optimal nutrient supply. Fertilisers are available as mineral fertilisers in the form of single (e.g. P-fertiliser), or multi component fertilisers (e.g. N, P, K-fertiliser) or as organic substrates such as compost, manure and sewage sludge. Above all, organic and some phosphorus fertilisers contain low amounts of inorganic (heavy metals) and organic pollutants. Organic micropollutants as antibiotics or hormones are found in substrates from wastewater treatment and animal manure.

Legislation attempts to minimise pollutant input to the agroecosystem. Additionally, it has set up threshold values that regulate both fluxes of pollutants per area and concentrations in fertilisers. However, as the number of potential hazardous substances is high and knowledge about their toxicity is limited, there is a tendency to restrict application of organic fertilisers. In Germany, the current legislation focuses on threshold values.

The objective of this research is to develop a tool that can calculate nutrient based pollutant fluxes. By this, different organic fertilisers become comparable in terms of their

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potential use and pollutant fluxes. This research does not take into consideration ecotoxicity and degradation processes in the environment.

Material and methods

The model was developed originally by Rieß (2003) for comparison of sewage sludge and manure. It compared only heavy metal fluxes. It was improved to evaluate organic pollutants and to analyse which organic substrates are suitable for a combined application of pig slurry, cattle slurry and human urine. The model is based on the assumption that a certain amount of nutrients and organic matter is required on a long term average for maintenance of soil fertility. The necessary inputs – each of them defined as one nutrient equivalent (NE) – are N: $170\,\mathrm{kg\,ha^{-1}}$, P: $26.4\,\mathrm{kg\,ha^{-1}}$, K: $132.8\,\mathrm{kg\,ha^{-1}}$, Ca: $177.5\,\mathrm{kg\,ha^{-1}}$, Mg: $18\,\mathrm{kg\,ha^{-1}}$, S: $20\,\mathrm{kg\,ha^{-1}}$ and humic substances: $1{,}500\,\mathrm{kg\,ha^{-1}}$. Thus, seven NEs are needed to supply arable fields with sufficient fertiliser. According to the concentrations of these nutrients in the substrates, one of them limits the application rate – otherwise the field would be over fertilised – and defines the application rate per hectare. This rate is used to calculate pollutant fluxes.

The data used in the model were collected by literature research and are presented in Table 1. For heavy metal concentrations and nutrients in manure, a large amount of data

Table 1 Overview about original data and its references used in the model

Nutrients	Pig manure (kg/t DM)	Reference	Cattle manure (kg/t DM)	Reference	Urine (kg/m^3)	Reference
Nitrogen	72	Rieß, 2003	40	Rieß, 2003	9.13	1,2,3
Phosphorus	22	Rieß, 2003	7.04	Rieß, 2003	0.77	1,2,3,4
Potassium	36.52	Rieß, 2003	45.65	Rieß, 2003	2.64	1,2,3,4
Calcium	12.78	Rieß, 2003	12.78	Rieß, 2003	0.2	1,2
Magnesium	8.4	Rieß, 2003	4.8	Rieß, 2003	0.11	1,2
Sulphur	2	Rieß, 2003	2	Rieß, 2003	1.08	Lentner, 1977
Humic substances	750	Rieß, 2003	750	Rieß, 2003	0	own observation
Heavy metals						
Cadmium	0.4	LABO, 2000	0.28	LABO, 2000	0.0018	Lentner, 1977
Chromium	9.4	LABO, 2000	7.3	LABO, 2000	0.0072	Lentner, 1977
Copper	309	LABO, 2000	44.5	LABO, 2000	0.0296	Lentner, 1977
Mercury	0.02	LABO, 2000	0.06	LABO, 2000	0.0043	Lentner, 1977
Nickel	10.3	LABO, 2000	5.9	LABO, 2000	0.0022	Lentner, 1977
Lead	6.2	LABO, 2000	7.7	LABO, 2000	0.0013	Vinnerås *et al.*, 2006
Zinc	858	LABO, 2000	270	LABO, 2000	0.3750	Lentner, 1977
Antibiotics						
Tetracycline	146	Engels, 2004	462	BLAC, 2003	0.002	calculated
Oxytetracycline	108	Engels, 2004	5.3	Patten *et al.*, 1980	0.023	calculated
Chlortetracycline	112	Engels, 2004	11.3	Patten *et al.*, 1980	0.001	calculated
Sulphamethazine	88	Engels, 2004	0	BLAC, 2003	–	
Sulphadiazine	68	Engels, 2004	20	BLAC, 2003	–	
Hormones						
Oestrone	4.728*	Hanselman *et al.*, 2003	0.543	Hanselman *et al.*, 2003	0.011	calculated
17α-Ethinyloestradiol	0.89*	Hanselman *et al.*, 2003	0.370	Hanselman *et al.*, 2003	0.0001	calculated
17ß-Oestradiol	1.215*	Hanselman *et al.*, 2003	0.239	Hanselman *et al.*, 2003	0.0089	calculated
Other pharmaceuticals						
Bezafibrate					0.315	calculated
Carbamazepine					0.116	calculated
Diclofenac					1.063	calculated
Ibuprofen					0.126	calculated
Primidone					0.046	calculated
Propyphenazone					0.067	calculated

–was not possible to calculate 1 Lentner, 1977 3 Jocham and Miller, 1994
*farrowing pit 2 Hofstetter and Eisenberger, 1996 4 Alken and Walz, 1998

is published (summarised in Rieß, 2003). Average nutrient values in urine were calculated by data published in four different investigations (Lentner, 1977; Jocham and Miller, 1994; Hofstetter and Eisenberger, 1996; Alken and Walz, 1998). Concentrations of heavy metals were mainly taken by Lentner (1977), besides lead which is taken from Swedish data (Vinnerås *et al.*, 2006). Values for micropollutants were collected by a literature review as well. The most relevant substances were chosen by their appearance in groundwater, mass of subscription and reported detection rates in animal slurry: tetracycline, oxytetracycline, chlortetracycline, sulphamethazine, sulphadiazine, oestrone, 17α-ethinyloestradiol, 17ß-oestradiol, bezafibrate, carbamazepine, diclofenac, ibuprofen, primidone and propyphenazone. The data for the three fertiliser types compared was selected in a way to represent a worst case scenario by using the maximum values. Data was directly available for pig and cattle slurry. This was not the case for urine. Here, theoretical concentration by definitive books and annual reports were used to quantify amounts. This is done in this rather complicated way as only few data sets of restricted user numbers have been analysed till now.

Hence, the calculation for the pharmaceuticals in urine was the following except for oestrone. The concentration in yellowwater was estimated via calculated data of consumed and renally excreted amounts (see eq.1).

$$\frac{\text{Consumed dose (g/a)} \times \text{Renal excretion (\%)}}{\text{Annual amount of urine in Germany (m}^3\text{/a)}} = \text{Concentration of pharmaceuticals in urine (g/m}^3\text{)} \tag{1}$$

Consequently, the annual amount of urine excreted in Germany was calculated to be $35{,}624 * 10^6\,\mathrm{m}^3\,\mathrm{a}^{-1}$. This takes into account an average volume of $1.22\,\mathrm{L}\ \mathrm{pers}^{-1}\,\mathrm{d}^{-1}$ of urine excreted (Lentner, 1977; Jocham and Miller, 1994; Hofstetter and Eisenberger, 1996) and the rounded number of 80 Mio inhabitants in Germany (Statistisches Bundesamt, 2006).

Theoretical annual amounts consumed were calculated by the yearly number of daily defined doses (DDDs (WHO, 2005)) times maximum daily dose. Therefore, the maximum was taken to receive a worst case scenario as already mentioned above. DDDs were taken from literature (Mutschler *et al.*, 2001; BPI, 2005; Fricke *et al.*, 2006; Goodman *et al.*, 2006) and annual prescribed number of DDDs from "Arzneiverordnungs-Report 2004" (Schwabe and Paffrath, 2004).

Moreover, the calculation of excreted amounts was achieved by two approaches. As a first step renal excretion data given in percent were applied directly. If these were not available renal excretion rates were calculated by means of Q_0 values. This value is defined as the non-renal elimination fraction, i.e. the percentage of the resorbed dose which is metabolised and excreted by other pathways than renally in unchanged form (Forth *et al.*, 2001). Therefore, the value $1 - Q_0$ is the fraction which is excreted unchanged via urine. In the Q_0 value, only the resorbed fraction is considered. Thus, for this calculation the ratio of resorption of each pharmaceutical in the human body was required. In some cases only semi-quantitative information existed. It was converted into numbers, e.g. "partly" is given as 33%.

As already mentioned, this calculation was not possible for oestrone as it is a natural hormone not taken in regular daily doses. It is excreted to 80% by women in the age of 15–64 years (CBS, 2002). D'Ascenzo (2003) reported a daily excretion rate in female urine of 32 μg pers^{-1} d^{-1}. In Germany live 27.1Mio women in the age between 15 and 64. Taking these facts into account an annual amount of 377 kg a^{-1} of oestrone is excreted via urine in Germany. Men were not considered in this calculation due to its low oestrogenic background (Fotsis *et al.*, 1980).

17ß-oestradiol is a natural hormone as well as a prescribed drug. Hence, its amount was calculated along both methods described in the two paragraphs above.

Results and discussion

Nutrients

The application rate of the three fertilisers was limited by different nutrients (Figure 1). In the case of urine it was limited by S. An amount of 19 m^3 ha^{-1} a^{-1} undiluted urine can be applied to match the nutrient demand. Then the NE for S was 1. The NE for N was almost 1 as well, but all other nutrients need to be added additionally to the field. When considering newest research (personal communication from Vinnerås and Oldenburg), S concentrations are around 0.3 mg L^{-1} and N 6.9 g L^{-1}. Taking this information into account, the amount of urine being field applied increases to 25 m^3 ha^{-1} a^{-1}. The application of pig slurry was limited by P (1.2 t DM ha^{-1} a^{-1}), the one of cattle slurry by humic substances (2 t DM ha^{-1} a^{-1}). For the slurries, only about 50% of the N-input was covered. The overall nutrient input reached its highest level by cattle slurry (3.6 NEs), followed by pig slurry with 3.2 NEs and then urine with 3.0 NEs. For the calculations of pollutant fluxes, application rates of 19 m^3 ha^{-1} a^{-1} were used for urine, 1.2 t DMha^{-1} a^{-1} for pig slurry, and 2 t DM ha^{-1} a^{-1} for cattle slurry.

The calculations are based on an average fertiliser dose which may vary considerably from crop to crop. For example, the sulphur demand of rape (60–70 kg ha^{-1} a^{-1}) is higher compared with cereals (30–40 kg ha^{-1} a^{-1}). In such a case, nitrogen would be the limiting factor. Consequently, a higher dose of urine would be applied. Moreover, higher doses might be useful for soils with nutrient deficiencies.

Nevertheless, legislation and farmers tend to consider only nitrogen, phosphorus, and potassium in their fertiliser management systems neglecting other nutrients. Then, potassium would restrict the application rate to 2.9 t DM a^{-1} in cattle slurry.

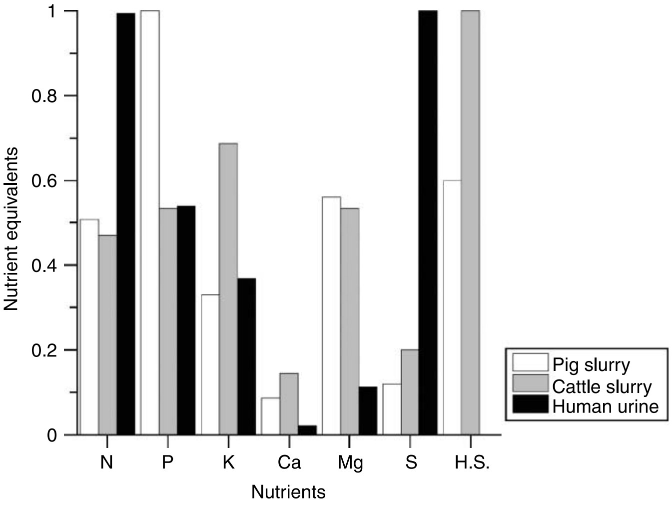

Figure 1 Limiting nutrient equivalents for pig and cattle slurry and urine. H.S.: humic substances

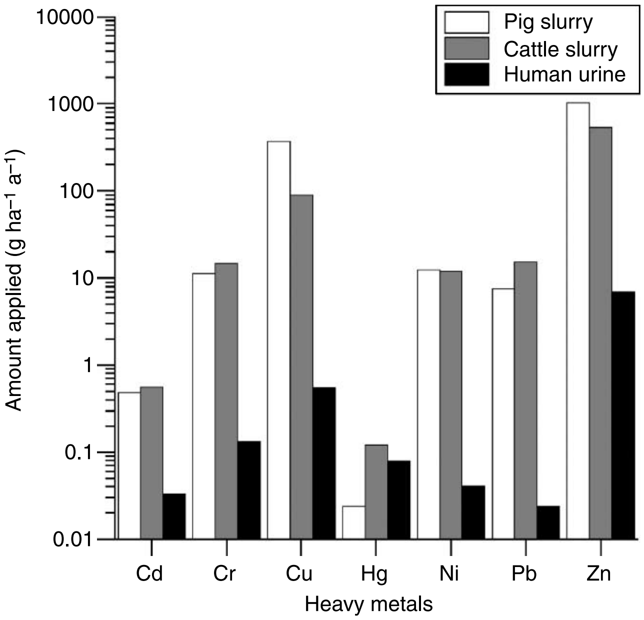

Figure 2 Heavy metal fluxes per hectare and year using the optimum fertiliser dosage of pig and cattle slurry as well as urine

Heavy metals

The model clearly showed that input of heavy metals by urine was only 10% or even less compared with animal slurry (Figure 2). Fluxes of Cu, Ni and Pb were more than 100 times higher by slurries. Only Hg presents a different pattern. At the low level of 0.08 g ha^{-1} a^{-1} urine induced Hg input was higher than by pig slurry (0.02 g ha^{-1} a^{-1}). Additionally, it has to be mentioned that Cu and Zn are micronutrients. For Zn, 100–300 g ha^{-1} a^{-1} and for Cu 50–100 g ha^{-1} a^{-1} are removed by crops. The high fluxes of Cu and Zn have been reported due to feed additives and medication (Kamphues, 1997; Kühnen *et al.*, 2001; Meyer, 2002).

Antibiotics

In general, the amounts of antibiotics (Figure 3) applied by urine were smaller than for pig and cattle slurry. However, the comparison is only valid for the group of tetracyclines, as data for sulphamethaxine and sulphadiazine from urine are missing. The highest flux of urine application was calculated for oxytetracycline (0.43 g ha^{-1} a^{-1}). Its flux was 4% of the flux reached by cattle slurry and only 0.3% when compared with pig slurry. Fluxes of antibiotics from pig slurry were always higher than cattle and urine besides tetracycline. The value of tetracycline applied by cattle slurry was 924 g ha^{-1} a^{-1}, the highest for antibiotics overall.

Hormones

Figure 4 clearly shows decreasing amounts of hormones from pig over cattle slurry to human urine. Here the flux of 17α-ethinyloestradiol holds the lowest input value of the calculated steroids for soils with 0.0012 g ha^{-1} a^{-1}. This is remarkable as it is dominating in contraceptives and causing wide effects in the aquatic environment (Daughton and Ternes, 1999;

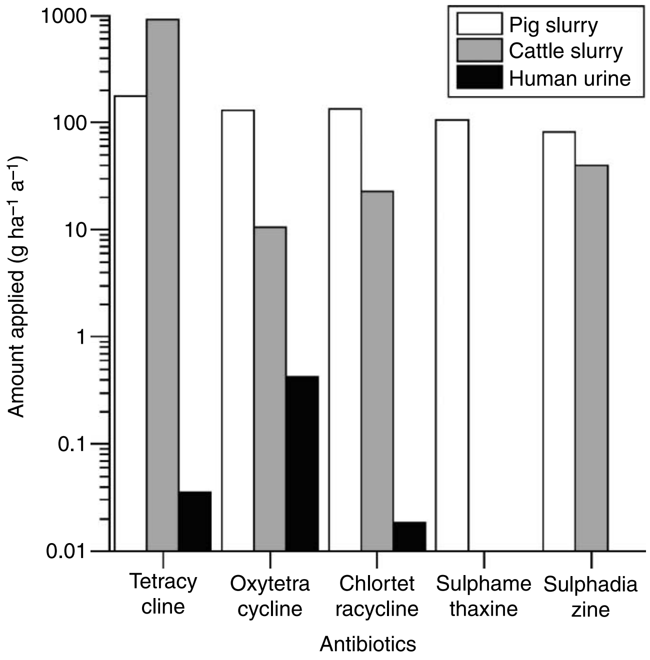

Figure 3 Antibiotic fluxes per hectare and year using the optimum fertiliser dosage of pig and cattle slurry as well as human urine

Birkett, 2003). Furthermore, it must be mentioned that hormone fluxes for pigs were measured in slurry of farrows which might explain the high value of oestrone especially.

Other pharmaceuticals

Other pharmaceuticals showed inputs lower than 20 g ha^{-1} a^{-1} (Table 2), with a highest input for diclofenac with 19.7 g ha^{-1} a^{-1}, although substances chosen are among those with the highest annual consumption rates in Germany (BLAC, 2003). A comparison

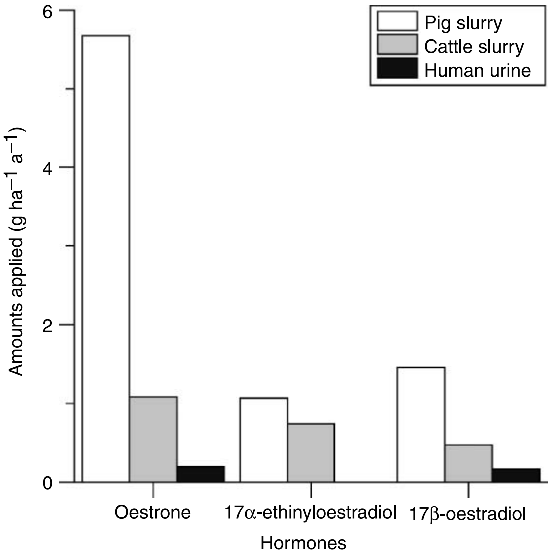

Figure 4 Steroid fluxes per hectare and year using the optimum fertiliser dosage of pig and cattle slurry as well as urine

Table 2 Fluxes of non-antibiotic pharmaceuticals per hectare and year based on the optimum fertiliser dosage of urine

	Bezafibrate	Carbamazepine	Diclofenac	Ibuprofen	Primidone	Propyphenazone
Flux (g ha^{-1} a^{-1})	5.8	2.2	19.7	2.3	0.9	5.6

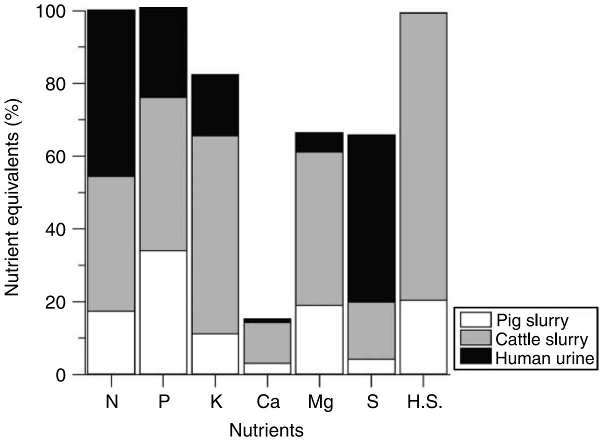

Figure 5 Maximum nutrient equivalents for combination of pig and cattle slurry with urine. H.S.: humic substances

between the different fertiliser products cannot be accomplished, as usage of these substances in animal health care is negligible.

An overall evaluation regarding the input of organic micropollutants such as hormones and pharmaceuticals needs to be based on toxicity studies. Also, studies on degradation, metabolite formation and their toxicity are necessary to judge the potential danger of the low but constant fluxes to arable soils.

Combination of different organic fertilisers

Based on the calculations of nutrient equivalents, a blend of all three fertilisers would result in the highest nutrient supply: 5.3 NEQs (Figure 5). This dosage implies 0.4 t DM of pig slurry, 1.6 t DM of cattle slurry and 8.5 m^3 of urine. Urine shows the lowest pollution level. Consequently, its combination with the slurries decreases the average pollutant fluxes by its diluting effect.

Moreover, the only possibility combining two fertilisers is an addition of urine to cattle slurry. The application of cattle slurry is limited by humic substances which urine does not contain.

Conclusions

The tool calculates possible combinations of different fertilisers as well as fluxes of pollutants. Neither single- nor multi-component application of animal slurry and urine can match the soil demand of nutrients; thus other fertilisers are needed in addition.

In general, heavy metals, antibiotics and hormones show higher values in animal manure then in human urine but additional loads by other pharmaceuticals consumed by human beings have to be considered in this substrate.

Ecotoxicological investigations are needed to determine their hazardousness in soil systems. Overall, the model is a suitable tool worth extending in aspects of hygiene and environmental impacts as, for example, degradation processes as well as ecotoxicology.

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