

# Organophosphorus Flame Retardants and Plasticizers in Swedish Sewage Treatment Plants

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The levels, distribution, and possible sources of 12 organophosphorus flame retardants and plasticizers, some of which are reported to be toxic to aquatic organisms, were investigated in samples of influents, effluents, and sludge from 11 Swedish sewage treatment plants (STPs). The organophosphorus compounds (OPs) studied were poorly removed from the wastewater; especially the chlorinated OPs tended to pass through the STPs without being removed or degraded, while alkyl-OPs, such as tributyl phosphate (TBP), were more successfully removed. In both influents and effluents, tris(2-butoxyethyl) phosphate and TBP were the most prominent substances followed by tris(2-chloroisopropyl) phosphate (TCPP). The highest concentration of any individual OP detected in the influents was  $52 \mu\text{g L}^{-1}$  (TBP). Ethylhexyl diphenyl phosphate and TCPP dominated in all sludge samples. A budget calculation comparing the annual amount of OPs in the influent received by Swedish STPs with the known amount of OPs imported indicated that approximately 15% is emitted to STPs. Of the total amount of OPs reaching the STPs annually, 49% is degraded, 50% (27 tons) is emitted to the recipients, and only 1% ends up in the sludge. The concentrations of most OPs were quite similar among the sampled STPs, indicating that the data may be applicable in other STPs.

## Introduction

Organophosphorus compounds (OPs) are frequently utilized as flame retardants and plasticizers, but they are also used as antifoaming agents and additives in products such as lubricants and hydraulic fluids. The global consumption of OPs amounted to 186 000 tons in 2001, and in recent years the consumption of OPs has increased sharply. For example, in the year 2001 West European consumption was estimated to amount to 83 000 tons, compared to 58000 tons in 1998, distributed evenly between chlorinated and nonchlorinated OPs (1, 2). TCPP, TDCPP, TEHP, TPP, TBEP, TBP, EHDPP, and TCEP (for abbreviations, see Table 2 in the Analysis subsection) dominated Swedish imports of OPs in the year 2003, with imported quantities ranging from 30 to 130 tons (3). Furthermore, TCEP is included in the European Commission second priority list (4), while TCPP and TDCPP are included in the fourth priority list (5). They are also listed as EU high production volume (HPV) chemicals together with TPP, TBP, TBEP, and EHDPP (6).

Apart from being used as additives in various plastic materials, OPs are also applied as plasticizers and flame

retardants in products such as paints, glues, lacquers, and varnishes. The chlorinated OPs are used in both flexible and rigid polyurethane foam (PUF), rubber, and textile coatings (7). Flexible foams are used in products such as upholstered furniture and mattresses, while rigid foams are used for thermal insulation. Some OPs, for example, TBP and TPP, are utilized as extreme pressure additives and/or antiwear agents in hydraulic fluids, lubricants, and transmission and motor oils to prevent surface damage (8). Apart from being a main ingredient in some fire-resistant hydraulic fluids, TBP is also used as a solvent for natural gums (9) and as an antifoaming agent in concrete (10). TBEP and TEHP are used as softeners in synthetic rubber and PVC to impart low-temperature flexibility and flame retardation (11). The broad application range of OPs and the fact that they are utilized as additives may result in their diffusive spreading into the environment by volatilization, leaching, and abrasion. Besides being ubiquitous substances in indoor environments (12), OPs have also been detected in dry and wet deposition (13, 14). Thus, OPs can be transferred to STPs via the sewage system from households, industrial sites, and drainage of stormwater.

OPs have previously been semiquantitatively determined in wastewater from a couple of Swedish STPs (15, 16). In 1992, influent levels ranging up to 2 and  $5.8 \mu\text{g L}^{-1}$  for TBP and TBEP, respectively, were reported, with corresponding levels in effluent up to 0.4 and  $0.6 \mu\text{g L}^{-1}$  (15). A couple of years later, the level of TBEP in effluent of the same STP was found to be  $28 \mu\text{g L}^{-1}$  (16). The maximum levels of the other OPs measured in the effluents were  $3 \mu\text{g L}^{-1}$  (TBP),  $4.0 \mu\text{g L}^{-1}$  (TCPP),  $3.0 \mu\text{g L}^{-1}$  (TDCPP), and  $3.0 \mu\text{g L}^{-1}$  (TPP). In studies from German STPs, TCPP and TBP have been found in influents and effluents at levels similar to those reported from Sweden, while the concentrations of TDCPP and TPP in effluents were an order of magnitude lower than in the Swedish STPs (17, 18). The concentrations of TCPP in influents have been found to show great day-to-day variation, with lower concentrations during weekends (18). Meyer and Bester also concluded that there was no elimination of the chlorinated OPs in the STPs (18). Similar observations have previously been reported for wastewater from a German STP by Fries and Püttmann, who found TCEP concentrations of  $21 \mu\text{g L}^{-1}$  in influent and  $34 \mu\text{g L}^{-1}$  in effluent (19).

Little is known about the toxicity and environmental effects of OPs. Of the triaryl and chlorinated phosphates, TPP and TDCPP seem to have the highest toxicity to aquatic organisms, with 96 h  $\text{LC}_{50}$  values of 0.36 and  $1.1 \text{ mg L}^{-1}$ , respectively, for rainbow trout (7, 20). TBP is about one order of magnitude less toxic ( $4.2\text{--}12 \text{ mg L}^{-1}$ ) to the same species (9). TCPP and TCEP are even less toxic to fathead minnow ( $51 \text{ mg L}^{-1}$ ) and goldfish ( $90 \text{ mg L}^{-1}$ ), respectively (7). Further, low to moderate acute oral toxicities have been reported for chlorinated OPs, TBP, and TEHP (7, 9, 11).

As mentioned above, OPs have previously been detected in STP samples. However, to the best of our knowledge, there have been no studies of the concentrations of multiple OPs in both wastewater and sludge from multiple STPs; usually only one or a few OPs or STPs have been studied. We have, therefore, measured 12 OPs focusing on those imported in the greatest quantities into Sweden, in influents, effluents, and sludge from 11 Swedish STPs of various sizes treating wastewater from various types of industrial plants. In addition, the data generated would be of great value for the risk assessments that are currently carried out within the European Union. In the present paper, we discuss the observed levels and OP profiles in relation to known sources

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**FIGURE 1.** Schematic map showing the locations of the 11 STPs included in the study.

and source patterns, as well as the results of mass balance estimations for Swedish STPs.

## Materials and Methods

**Chemicals.** All solvents used were of analytical grade. Dichloromethane (DCM) was purchased from B&J, Fluka Chemie (Buchs, Switzerland), acetone, toluene, ethyl acetate, cyclohexane, 2-propanol, *n*-hexane, silica gel 60 (0.040–0.063 mm), and sodium sulfate were purchased from Merck (Darmstadt, Germany), ethanol (99.5%) was purchased from Kemetyl (Haninge, Sweden), dichloroethane (DCE) was purchased from BDH (Poole, U.K.), and diatomaceous earth (acid-washed) was purchased from MP Biomedicals Inc. (Aurora, OH). Biobeads S-X3 (200–400 mesh) were obtained from Bio-Rad Laboratories Inc. (Hercules, CA). The OPs were of technical grade unless otherwise stated. Ethyl parathion (98.5%) and musk xylene-*d*<sub>15</sub> were purchased from Dr. Ehrenstorfer (Augsburg, Germany), tributyl phosphate (p.a.), triphenyl phosphate (99%), and tris(2-chloroethyl) phosphate (97%) were purchased from Labora (Sollentuna, Sweden), and tris(2-butoxyethyl) phosphate (94%) and tris(2-ethylhexyl) phosphate (97%) were purchased from Sigma-Aldrich (St. Louis, MO). Trimethyl phosphate, tripropyl phosphate, tripentyl phosphate, and di-*n*-octylphenyl phosphate were obtained from Stockholm University (Sweden). The European Flame Retardants Association (EFRA) kindly donated tris-(chloropropyl) phosphate and tris(1,3-dichloro-2-propyl) phosphate through Safe Pharm Laboratories (Derby, U.K.).

**Sampling.** Samples were collected, in extensively cleaned glass bottles, from 11 STPs, spread across Sweden (Figure 1). The STPs were chosen to represent small STPs with negligible industrial loads, medium-sized STPs receiving water from large industrial sites, and large STPs serving big cities. Descriptive data regarding size, treatment processes and flows, etc. for each STP are given in Table 1. Influent, effluent, and sludge were collected from STPs 1–7, and only sludge was collected from STPs 8–11. The aim was to collect all samples under normal operating conditions. However, we learned that there were disturbances in the sedimentation process in STP 5 during the sampling week, which would have influenced the OP levels in its effluent. Thus, no data on the OP levels in its effluent will be reported here.

Water samples, representing weekly averages, were collected flow proportionally using the automatic sampling equipment installed at each STP, except at the smallest STPs (1 and 5), in which the sampling was performed manually three times a day during the sampling week. Duplicate samples were collected at STPs 2 and 4 (with a 3 day interval

at STP 2). The sludge at each STP was usually sampled by collecting three composite samples of the final product at the end of the treatment process during the same week that the wastewater was collected. However, at STPs 2 and 4 sludge samples were collected a couple of weeks later than the wastewater. All sludge samples collected were anaerobically digested, except at STPs 1, 5, and 9. At STPs 1 and 5, there is no biological treatment of the wastewater, and furthermore, the sludge collected at STP 5 had been dewatered and stored outdoors for 4–6 months; at STP 9 the sludge was aerobically stabilized. To reduce the risk of microbial degradation, the wastewater and sludge samples were frozen immediately after sampling and stored in a freezer (–18 °C) until the time of analysis.

**Sample Preparation. Wastewater.** One liter of each influent and effluent sample was filtered (Munktell filter paper, 20 cm diameter, coarseness 3) into a 2.5 L separator funnel. Tripentyl phosphate (TPeP; 400 ng), dissolved in 1 mL of ethanol, was added to each sample as an internal standard (IS). The samples were then extracted by vigorous shaking with 100, 40, and 25 mL of DCM (5 min each). The first portion of DCM was passed through the same filter as the sample to release OPs that may have been attached to particles trapped by the filter. The organic layers were combined, evaporated to 2 mL by rotary evaporation, dried in columns packed with anhydrous sodium sulfate, and evaporated under a gentle stream of nitrogen. The solvent was changed to DCE, and the volume was adjusted to 1 mL. The final sample volumes were determined gravimetrically.

The efficiency of the liquid–liquid extraction has previously been evaluated in a recovery test in which three samples of 2 L of Milli-Q water were each spiked with 12 OPs (350–530 ng/OP) and extracted with DCM as described elsewhere (14). Recoveries of the individual OPs ranged from 81% to 100% except for TMP, for which 47% was recovered.

**Sludge.** The sludge samples were freeze-dried and then prepared and analyzed at the University of Duisburg-Essen, Germany, following a method developed and evaluated by Andresen and Bester (personal communication, 2004). Six of the eleven sludge samples (from STPs 1–4, 7 and 8) were analyzed in duplicate after approximately 5 g of each sample and 6 g of acid-washed diatomaceous earth were homogenized in a batch homogenizer (IKA A11 Basic (IKA Works, Guangzhou, People's Republic of China) and then transferred to 33 mL Dionex accelerated solvent extractor (ASE) cells fitted with a Dionex D28 filter. If needed, additional diatomaceous earth was used to fill up the cells. Between samples, the homogenizer was cleaned with 3 × 100 mL of 2-propanol. The samples were then extracted with 50 mL of ethyl acetate (90 °C, 150 bar) using a Dionex ASE 200 system (Sunnyvale, CA), and 100 ng of deuterated musk xylene-*d*<sub>15</sub> (*d*<sub>15</sub>-MX) was added to each sample as an internal standard. The samples were evaporated to 1 mL using a Büchi syncore evaporator (60 °C, 240 bar), and the solvent was changed by adding 10 mL of cyclohexane/ethyl acetate (1:1) and reducing the volume to 1 mL by evaporation. The concentrated samples were then filtered through 0.45 μm PTFE membranes (Alltech Associates Inc., Deerfield, IL) to remove particles before cleanup, using gel permeation chromatography (GPC). The GPC system included a GPC Basix equipped with a GPC 1122 solvent delivery system (LCTech GmbH, Dorfen, Germany) and a 25 × 400 mm glass column containing 50 g of Biobeads SX-3. The GPC system was eluted with ethyl acetate/cyclohexane (1:1) at a flow rate of 5 mL min<sup>-1</sup>. Three fractions were collected, 0–20, 20–42, and 42–62 min, each of which was evaporated to 1 mL. The middle fractions, which contained the analytes of interest, were further cleaned using 6 mL glass columns packed with 1 g portions of dry silica (105 °C, 24 h). Each column was conditioned with 8 mL of hexane before the sample was added and then eluted with

**TABLE 1. Descriptive Data for the Investigated Sewage Treatment Plants**

|   | influent, effluent, and sludge samples |        |        |        |       |        |        | sludge samples |       |        |        |
|---|--|--------|--------|--------|-------|--------|--------|----------------|-------|--------|--------|
|   | 1                                      | 2      | 3      | 4      | 5     | 6      | 7      | 8              | 9     | 10     | 11     |
| size  | small                                  | large  | medium | large  | small | medium | medium | medium         | small | large  | medium |
| treatment <sup>a</sup>                                    | M/C                                    | M/C/B  | M/C/B  | M/C/B  | M/C   | M/C/B  | M/C/B  | M/C/B          | M/C/B | M/C/B  | M/C/B  |
| sampling year   | 2003                                   | 2002   | 2003   | 2002   | 2003  | 2003   | 2003   | 2003           | 2003  | 2003   | 2003   |
| sampling week, water                                      | 5 and 6                                | 9      | 4      | 5      | 42    | 19     | 40     |                |       |        |        |
| sampling week, sludge                                     | 5 and 6                                | 10–12  | 4      | 7–9    | 42    | 19     | 40     | 49             | 49    | 49     | 49     |
| no. of personal equivalents                               | 3400                                   | 257000 | 102000 | 695000 | 1500  | 32500  | 30400  | 24000          | 9800  | 775000 | 104000 |
| flow (10 <sup>3</sup> m <sup>3</sup> year <sup>-1</sup> ) | 756                                    | 44900  | 14500  | 88000  | 182   | 3750   | 4730   | 4500           | 1500  | 107000 | 11200  |
| sampling flow (m <sup>3</sup> day <sup>-1</sup> )         | 4700                                   | 140900 | 46100  | 317500 | 500   | 10300  | 14900  |                |       |        |        |
| sludge dw (tons year <sup>-1</sup> )                      | 170                                    | 5800   | 3500   | 13900  |       | 790    | 770    | 800            | 240   | 14400  | 1900   |

<sup>a</sup> M = mechanical, C = chemical, and B = biological treatment (activated sludge).

8 mL of ethyl acetate (fraction 1) followed by 8 mL of acetone (fraction 2, control). All ethyl acetate fractions, which contained OPs, were evaporated into 1 mL of toluene and transferred to 2 mL vials.

The efficiency of the method applied was evaluated by a recovery test, in which 10 g samples of a 1:1 mixture of manure and soil were homogenized and spiked with OPs at eight concentrations ranging from 3 to 10 000 ng g<sup>-1</sup> (three replicates per level). The samples were extracted and cleaned as described above. Individual recoveries ranged from 93% to 117% with a relative standard deviation of 16–20% (Andresen and Bester, personal communication).

**Blanks.** A portion of DCM was concentrated 1500-fold by rotary evaporation, and 1  $\mu$ L of the concentrated solvent was analyzed by gas chromatography with a nitrogen phosphorus detector (GC-NPD) as described below for the wastewater samples. The chromatogram obtained showed no significant differences from a chromatogram of virgin solvent. Similarly, no OPs were detected when 10 g of sodium sulfate was checked for contamination by eluting with DCM, concentrating the solvent, and analyzing 1  $\mu$ L by GC-NPD. Thus, no contaminants were introduced during extraction and cleanup of the wastewater samples. Furthermore, two diatomaceous earth blanks, one of which was homogenized, were processed in parallel to the sludge samples (blanks 1 and 2, Table 4).

**Analysis.** The wastewater samples were analyzed using a GC-NPD system consisting of an HP 5890 GC instrument equipped with an HP 7673 autosampler (Hewlett-Packard, Avondale, PA) and ChemStation, version A.10.01, software (Agilent Technologies). Gas chromatographic separation was carried out on a DB-5 MS fused silica capillary column (length 30 m, i.d. 0.25 mm, film thickness 0.25  $\mu$ m) from J&W Scientific (Folsom, CA). The injector temperature was set to 250 °C and the detector temperature to 300 °C. Analysis was initiated by injecting 1  $\mu$ L aliquots in splitless mode, 2 min splitless time. The GC oven was initially held at 40 °C for 4 min and increased to 190 °C at a rate of 15 °C min<sup>-1</sup> and then at 10 °C min<sup>-1</sup> to the final temperature, 310 °C, which was maintained for 4 min. Helium was used as carrier gas at a flow rate of 1.5 mL min<sup>-1</sup>. The gas flows to the NPD were set as follows: air, 100 mL min<sup>-1</sup>; hydrogen, 3.7 mL min<sup>-1</sup>; helium makeup gas, 30 mL min<sup>-1</sup>.

To verify the identity of OPs found in the wastewater, selected samples were reanalyzed by GC–mass spectrometry (GC–MS). The analyses were performed using a GC 8000 Top (ThermoQuest, Milan, Italy) coupled to a Fisons MD 800 mass spectrometer (Manchester, U.K.), using the same oven temperature program and type of column as in the GC-NPD analyses. The injected volume was 1  $\mu$ L. Helium was used as carrier gas at a flow of 1.5 mL min<sup>-1</sup>. Analytes eluting from the column were introduced directly into the ion source (200 °C) via a heated transfer line (250 °C). The MS instrument was operated with electron impact (EI) ionization at 70 eV ionization energy, and full-scan spectra

were collected over the *m/z* range 25–440. For positive identification of a candidate compound two criteria had to be fulfilled: (i) the retention time had to be within 5 s of the standard, and (ii) the spectral match had to be above 700 (NIST library, reverse search), or if the standard spectrum match was poor, the spectral match had to be within 200 units of the corresponding standard, and several abundant characteristic fragment ions had to be observed.

The sludge samples were analyzed using another GC–MS system (Thermo Finnigan DSQ, Dreieich, Germany) equipped with a programmed temperature vaporizing (PTV) injector. One  $\mu$ L of each sample was injected into the PTV, which was operated in splitless mode (1 min splitless time), and its temperature was ramped as follows: 115 °C for 0.05 min, increased at 12 °C s<sup>-1</sup> to 280 °C, which was held for 1 min, and then at 5 °C s<sup>-1</sup> to 320 °C, held for 15.5 min (cleaning phase). GC was performed using the same type of column as described for the GC-NPD analyses. The oven temperature was held at 100 °C for 1 min and then increased to 130 °C at a rate of 30 °C min<sup>-1</sup> followed by 8 °C min<sup>-1</sup> to 220 °C, and finally at 30 °C min<sup>-1</sup> to the final temperature, 280 °C, which was held for 7 min. Helium was used as carrier gas at 1.3 mL min<sup>-1</sup>. The temperature of the transfer line was 250 °C, the ion source was set to 200 °C, and the MS instrument was operated in selected ion monitoring (SIM) mode with EI at 70 eV.

**Calibration, Quantification, and Limits of Detection.**

The OPs were identified by comparisons of the retention times of sample components and reference standards, and the quantifications were performed using the internal standard technique, which automatically corrects the data for losses during sample workup and analysis. No correction was made for differences in recovery between individual OPs and the IS. However, this will only significantly affect the data for TMP, which will be underestimated, as it had a recovery of 47% in the method evaluation. A volumetric standard, ethyl parathion (200 ng), was added to each sample prior to analysis (RS) and was used to calculate the recovery of the internal standard, which ranged between 78% and 95% in the wastewater samples.

Single-point calibration was used after it had been proven that the GC-NPD responses were linear (correlation coefficients  $\geq 0.997$ ) over the interval 10–1500 pg  $\mu$ L<sup>-1</sup>. Each sludge sample was injected twice, and quantification was based on the peak areas of the two ions monitored for each substance (Table 2). Because of matrix interferences, TtBP was quantified against one ion. In more than 90% of the cases, the two injections resulted in similar values ( $\pm 20\%$  each) for TCPP, TDCPP, TBEP, EHDPP, and TPP. However, for TBP and TCEP, variations up to 59% were observed.

The average limit of detection (LOD), defined as 3 times the noise level, was 1.8 ng L<sup>-1</sup> and ranged between 0.8 and 2.9 ng L<sup>-1</sup> for the individual OPs in the wastewater samples. The corresponding LODs and range for sludge samples were

**TABLE 2. Abbreviations and CAS Numbers of the Analyzed Organophosphorus Compounds and the Ions Used for MS Quantification of OPs in the Sludge Samples**

| compound   | abbrev        | CAS no.    | quantification ions ( <i>m/z</i> ) |     |
|--|---------------|------------|------------------------------------|-----|
| trimethyl phosphate <sup>a</sup>                 | TMP           | 512-56-1   |                                    |     |
| tripropyl phosphate <sup>a</sup>                 | TPrP          | 513-08-6   |                                    |     |
| tributyl phosphate                               | TBP           | 126-73-8   | 155                                | 211 |
| tri- <i>iso</i> -butyl phosphate <sup>b</sup>    | T <i>i</i> BP | 126-71-6   | 155                                | 211 |
| tris(chloropropyl) phosphate <sup>c</sup>        | TCPP          | 13674-84-5 | 277                                | 279 |
| tris(2-chloroethyl) phosphate                    | TCEP          | 115-96-8   | 249                                | 251 |
| tris(1,3-dichloro-2-propyl) phosphate            | TDCPP         | 13674-87-8 | 379                                | 381 |
| triphenyl phosphate                              | TPP           | 115-86-6   | 325                                | 326 |
| tris(2-butoxyethyl) phosphate                    | TBEP          | 78-51-3    | 199                                | 299 |
| tris(2-ethylhexyl) phosphate <sup>a</sup>        | TEHP          | 78-42-2    |                                    |     |
| 2-ethylhexyl diphenyl phosphate <sup>b</sup>     | EHDPP         | 1241-94-7  | 251                                | 362 |
| di- <i>n</i> -octylphenyl phosphate <sup>a</sup> | DOPP          | 6161-81-5  |                                    |     |

<sup>a</sup> Substance only analyzed in wastewater samples. <sup>b</sup> Substance only analyzed in sludge samples. <sup>c</sup> The commercial mixture of TCPP contains four isomers, tris(2-chloroisopropyl) phosphate being the most abundant.

**TABLE 3. Levels (ng L<sup>-1</sup>) of OPs in Influent (In) and Effluent (Eff) from Various Swedish Municipal STPs<sup>a</sup>**

| STP | sample | TBEP     | TBP      | TCPP <sup>b</sup> | TCEP     | TDCPP    | TPP      | TMP      | TEHP     | DOPP     | total    |
|-----|--------|----------|----------|-------------------|----------|----------|----------|----------|----------|----------|----------|
| 1   | In     | 35000    | 13000    | 1800              | 290      | 250      | 76       | 584      | <1.4     | 218      | 51000    |
|     | Eff    | 30000    | 6100     | 2200              | 460      | 270      | 54       | <0.8     | <1.4     | <3.1     | 39000    |
| 2:1 | In     | 13000    | 52000    | 2900              | 90       | 450      | 230      | 350      | 74       | <3.1     | 69000    |
|     | Eff    | 11000    | 730      | 1800              | 470      | 180      | 100      | 57       | <1.4     | <3.1     | 14000    |
| 2:2 | In     | 11000    | 17000    | 1600              | 420      | 310      | 290      | 140      | <1.4     | <3.1     | 31000    |
|     | Eff    | 11000    | 1400     | 1700              | 450      | 180      | 130      | <0.8     | <1.4     | <3.1     | 15000    |
| 3   | In     | 20000    | 7400     | 3400              | 520      | 380      | 220      | <0.8     | <1.4     | 2 000    | 32000    |
|     | Eff    | 7800     | 4800     | 2400              | 470      | 240      | 58       | <0.8     | <1.4     | <3.1     | 16000    |
| 4:1 | In     | 9400     | 7900     | 2800              | 600      | 330      | 180      | 570      | 57       | <3.1     | 22000    |
|     | Eff    | 5700     | 4000     | 1500              | 350      | 130      | 53       | 79       | <1.4     | <3.1     | 12000    |
| 4:2 | In     | 7100     | 12000    | 1500              | 370      | 210      | 120      | 200      | 130      | <3.1     | 22000    |
|     | Eff    | 5300     | 4200     | 1600              | 410      | 150      | 57       | <0.8     | <1.4     | <3.1     | 12000    |
| 5   | In     | 8800     | 6600     | 1100              | 390      | 240      | 210      | <0.8     | <1.4     | <3.1     | 17000    |
|     | Eff    | <i>c</i> | <i>c</i> | <i>c</i>          | <i>c</i> | <i>c</i> | <i>c</i> | <i>c</i> | <i>c</i> | <i>c</i> | <i>c</i> |
| 6   | In     | 5300     | 30000    | 18000             | 1000     | 310      | 150      | <0.8     | <1.4     | <3.1     | 55000    |
|     | Eff    | 3100     | 780      | 24000             | 890      | 340      | 41       | <0.8     | <1.4     | <3.1     | 29000    |
| 7   | In     | 5200     | 24000    | 2500              | 530      | 320      | 130      | <0.8     | <1.4     | <3.1     | 33000    |
|     | Eff    | 4400     | 360      | 2300              | 530      | 310      | 76       | <0.8     | <1.4     | <3.1     | 7900     |

<sup>a</sup> Average of duplicate injections. Descriptive data for STPs 1–7 are given in Table 1. <sup>b</sup> Sum of three isomers: tris(2-chloroisopropyl) phosphate, CAS 13674-84-5; bis(2-chloro-1-methylethyl)(2-chloropropyl) phosphate, CAS 76025-08-6; 2-chloro-1-methylethyl bis(2-chloropropyl) phosphate, CAS 76649-15-5. <sup>c</sup> No data given as the plant was not operating properly.

1.8 and 0.2–5.1 ng g<sup>-1</sup>, respectively. On the basis of three replicate injections of four wastewater samples, the relative standard deviation was less than 10% for all analyzed OPs.

## Results and Discussion

**Wastewater.** TBEP and TBP were the most abundant OPs in both the influents and effluents (Table 3 and Figure 2). In the influents, the concentrations ranged from 5.2 to 35 μg L<sup>-1</sup> and from 6.6 to 52 μg L<sup>-1</sup> for TBEP and TBP, respectively. Corresponding levels for the same substances in the effluents ranged between 3.1 and 11 μg L<sup>-1</sup> and between 0.36 and 6.1 μg L<sup>-1</sup>. Similar levels have been reported in the influents of German STPs (13, 19).

The average levels of TCPP, TCEP, TDCPP, and TPP in the effluents were 4.4, 0.47, 0.31, and 0.08 μg L<sup>-1</sup>, respectively, similar to or slightly lower than corresponding levels reported from Germany (18). The levels in the effluent are expected to fluctuate less than in the influent due to the extensive mixing of the wastewater in the treatment process. Nevertheless, in some cases in the current study the chlorinated OPs were found at higher concentrations in the effluents than the influents. Such day-to-day variations have, for instance, been reported for TCPP (18, 21).

Generally, the levels were quite constant across the STPs studied, which is indicative of diffuse sources, suggesting emission of OPs from products used in both private

households and industry. Other diffuse sources, in cases when STPs receive drainage of streets (stormwater), are dry and wet deposition. The relatively high levels of TBEP found may, for example, be explained by the general use of TBEP-containing products. TBEP is used as an ingredient in floor polish and floor waxes, and has been shown to be the most abundant OP in indoor dust at levels ranging from 0.014 to 5.3 g kg<sup>-1</sup> (22). It probably reaches sewers via cleaning water from both public and domestic buildings. In some cases, however, elevated levels of individual OPs could be traced to possible point sources. For example, STP 6 had one order of magnitude higher levels of TCPP, in both its influent (18 μg L<sup>-1</sup>) and its effluent (24 μg L<sup>-1</sup>), than the other STPs. A factory that manufactures flame-retardant paints is connected to this STP, which may explain the elevated levels in the influent. Further, a major airport may be the source of elevated levels of TBP (52 μg L<sup>-1</sup>) in the influent of STP 2. TBP is widely used in aircraft hydraulic fluids, and has previously been found at high levels (25 μg kg<sup>-1</sup>) in snow samples from an airport (14).

**Sludge.** The total amounts of OPs in sludge varied between 0.6 and 7 μg g<sup>-1</sup> (dry weight). As for the wastewater, total and relative concentrations of most OPs did not show much variation between the STPs (Table 4 and Figure 3), except at the smallest STPs (1 and 5: 3400 and 1500 personal equivalents, respectively) where the observed levels of all

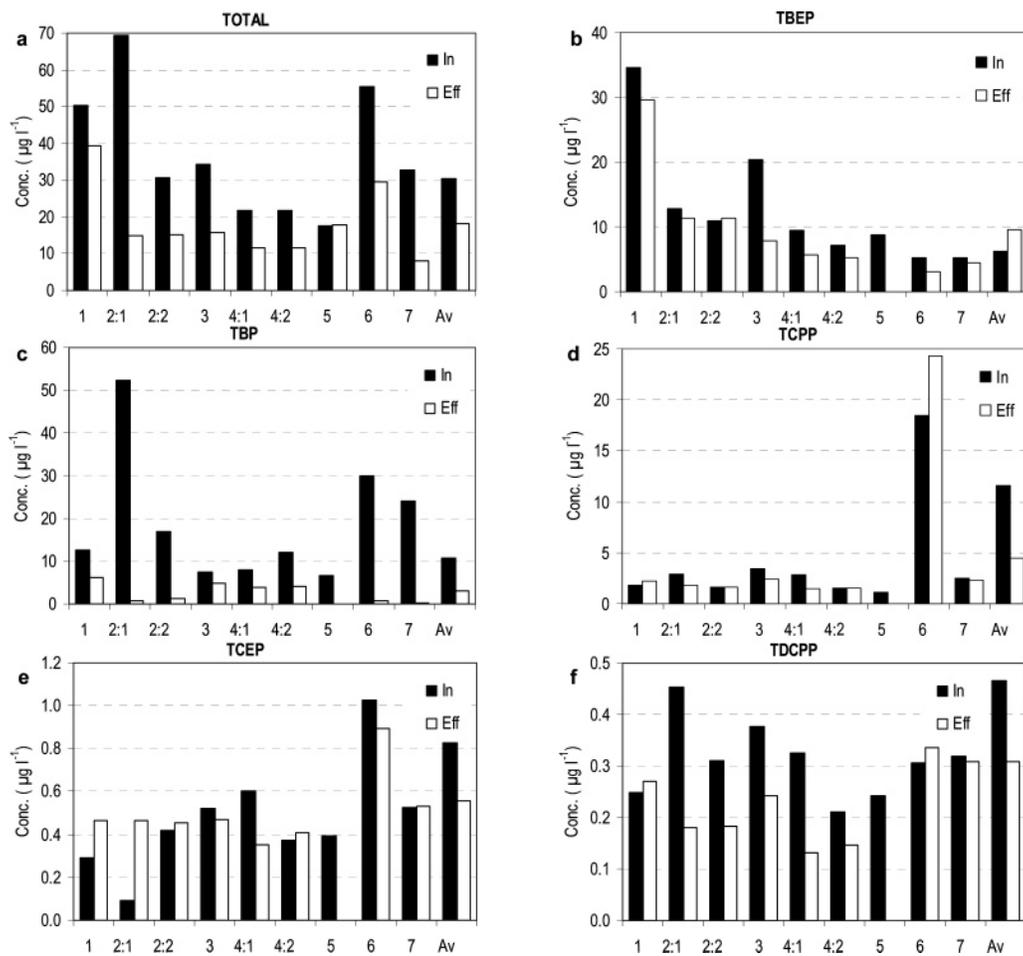


FIGURE 2. Concentrations of the total amount of OPs (a) and of the most frequently occurring OPs (b–f) in influent (In) and effluent (Eff) from various STPs. “Av” shows the average value. STPs 1–7 are described in Table 1.

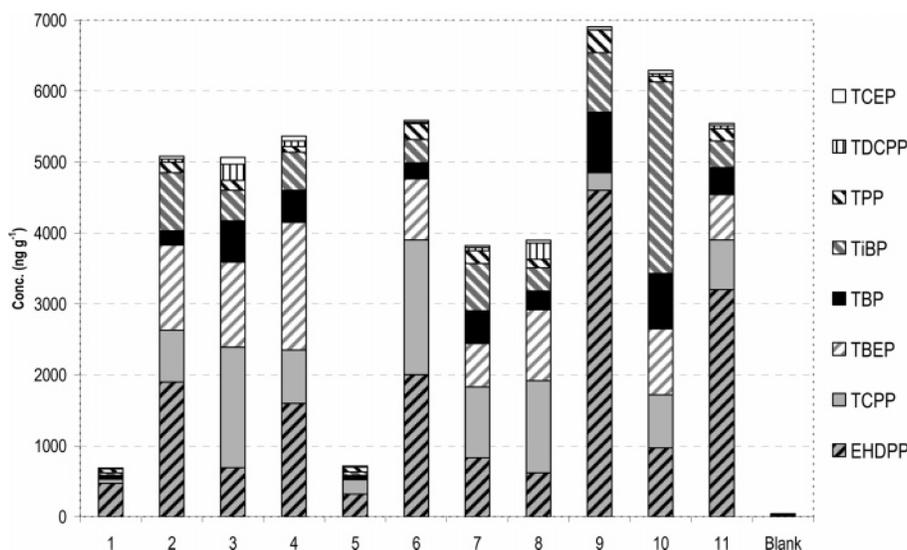
TABLE 4. Concentrations (ng g<sup>-1</sup> dw) of OPs in Sewage Sludge from Various Swedish Municipal STPs<sup>a</sup>

| STP     | EHDPP | TCPP | TBEP | TiBP | TBP | TPP | TDCPP | TCEP | total |
|---------|-------|------|------|------|-----|-----|-------|------|-------|
| 1:1     | 420   | 64   | <5.1 | 27   | 39  | 64  | 3.3   | 6.6  | 620   |
| 1:2     | 520   | 61   | <5.1 | 40   | 63  | 52  | 3.4   | 7.2  | 750   |
| 2:1     | 2300  | 850  | 1100 | 1000 | 240 | 190 | 49    | 46   | 5800  |
| 2:2     | 1400  | 610  | 1200 | 650  | 160 | 100 | 35    | 30   | 4200  |
| 3:1     | 690   | 1900 | 1900 | 340  | 600 | 130 | 220   | 82   | 5900  |
| 3:2     | 680   | 1500 | 560  | 530  | 570 | 140 | 230   | 110  | 4300  |
| 4:1     | 1500  | 650  | 1900 | 550  | 510 | 79  | 92    | 69   | 5400  |
| 4:2     | 1700  | 840  | 1700 | 540  | 380 | 72  | 75    | 62   | 5400  |
| 5       | 320   | 200  | <5.1 | 27   | 65  | 68  | 3.0   | 14   | 700   |
| 6       | 2000  | 1900 | 860  | 180  | 230 | 220 | 21    | 24   | 5400  |
| 7:1     | 660   | 790  | 740  | 180  | 280 | 170 | 11    | 10   | 2800  |
| 7:2     | 1000  | 1300 | 480  | 700  | 650 | 180 | 76    | 45   | 4400  |
| 8:1     | 580   | 1200 | 990  | 300  | 230 | 110 | 190   | 36   | 3600  |
| 8:2     | 650   | 1300 | 1100 | 360  | 280 | 120 | 260   | 35   | 4100  |
| 9       | 4600  | 250  | <5.1 | 840  | 850 | 320 | 7.3   | 37   | 6900  |
| 10      | 970   | 750  | 930  | 2700 | 780 | 77  | 40    | 48   | 6300  |
| 11      | 3200  | 700  | 640  | 380  | 380 | 170 | 41    | 33   | 5500  |
| blank 1 | 2.8   | <1.4 | <5.1 | 21   | 18  | 7.5 | 3.5   | 0.7  | 54    |
| blank 2 | 1.9   | <1.4 | <5.1 | 9.8  | 9.6 | 4.4 | 2.2   | 0.6  | 28    |

<sup>a</sup> Average of duplicate injections. Descriptive data for STPs 1–11 are given in Table 1.

the OPs were one order of magnitude lower than at the other STPs. Low amounts (0.6–21 ng g<sup>-1</sup>) of some of the analyzed substances were found in the laboratory blanks (Table 4), which can be considered negligible for most of the samples. However, in the sludge from STPs 1 and 5 the detected levels of TiBP, TBP, and TDCPP were similar to those in the blanks, so the uncertainties for these values are high.

In sludge, EHDPP (0.32–4.6 µg g<sup>-1</sup>), TCPP (0.06–1.9 µg g<sup>-1</sup>), and TBEP (0–1.9 µg g<sup>-1</sup>) were the most abundant OPs, followed by TBP, TiBP, TPP, and TDCPP. The highest levels of the chlorinated OPs (TCPP, TCEP, and TDCPP) were found at STPs 3 and 6. A factory manufacturing flame-retardant paints is connected to STP 6, as mentioned above, and a factory processing flexible PUF is connected to STP 3. In



**FIGURE 3.** Average levels and distribution patterns of OPs in sludge samples collected at 11 STPs and in blanks. Descriptive data for STPs 1–11 are given in Table 1.

**TABLE 5.** Estimated Annual Amounts and Degradation (Degr) of OPs, Calculated from Mean and Median Values, Respectively, of the Individual Concentrations of OPs in Influent (In), Effluent (Eff), and Sludge from Swedish Municipal STPs

|       | mean          |                |                        |                   |                           |                       | median        |                |                        |                   |                           |                       |
|-------|---------------|----------------|------------------------|-------------------|---------------------------|-----------------------|---------------|----------------|------------------------|-------------------|---------------------------|-----------------------|
|       | In amt (tons) | Eff amt (tons) | [Eff] <sup>a</sup> (%) | sludge amt (tons) | [sludge] <sup>b</sup> (%) | degr <sup>c</sup> (%) | In amt (tons) | Eff amt (tons) | [Eff] <sup>a</sup> (%) | sludge amt (tons) | [sludge] <sup>b</sup> (%) | degr <sup>c</sup> (%) |
| TBEP  | 19            | 15             | 77                     | 0.18              | 0.95                      | -20                   | 14            | 10             | 72                     | 0.21              | 1.5                       | -27                   |
| TBP   | 28            | 4.2            | 15                     | 0.09              | 0.34                      | -85                   | 20            | 4.1            | 21                     | 0.09              | 0.5                       | -79                   |
| TCPP  | 5.9           | 7.0            | 120                    | 0.20              | 3.4                       | +21                   | 3.8           | 3.0            | 80                     | 0.18              | 4.8                       | -15                   |
| TCEP  | 0.70          | 0.76           | 110                    | 0.01              | 1.3                       | +9                    | 0.63          | 0.70           | 110                    | 0.01              | 1.4                       | +12                   |
| TDCPP | 0.47          | 0.34           | 72                     | 0.02              | 3.4                       | -24                   | 0.47          | 0.32           | 68                     | 0.01              | 2.1                       | -30                   |
| TPP   | 0.27          | 0.11           | 40                     | 0.03              | 13                        | -47                   | 0.27          | 0.09           | 32                     | 0.03              | 12                        | -56                   |
| total | 54            | 27             | 50                     | 0.53              | 0.98                      | -49                   | 39            | 18             | 46                     | 0.53              | 1.4                       | -52                   |

<sup>a</sup> Formula used: (Eff amt/In amt) × 100. <sup>b</sup> Formula used: (sludge amt/In amt) × 100. <sup>c</sup> Formula used: [(sludge amt + Eff amt - In amt)/In amt] × 100.

addition, analysis of a sample of water used to clean the floors at the PUF factory indicated the presence of all three chlorinated OPs, with TDCPP at the highest levels (10 mg L<sup>-1</sup>). Thus, this factory clearly contributes to the levels detected at STP 3.

**Removal.** The distribution patterns of OPs in sludge and water are dependent on (i) the load of OPs in the influent, (ii) the partitioning of OPs between water and sludge, and (iii) the persistence of the OPs. In general, OPs have low to moderate solubility in water. For the most abundant OPs found in wastewater in the current study, the water solubilities are 1100 mg L<sup>-1</sup> (TBEP), 280 mg L<sup>-1</sup> (TBP), 1200 mg L<sup>-1</sup> (TCPP), 7000 mg L<sup>-1</sup> (TCEP), 7 mg L<sup>-1</sup> (TDCPP), and 1.9 mg L<sup>-1</sup> (TPP) (6). However, other substances present in wastewater, such as detergents and dissolved organic matter, are likely to increase the fraction of OPs in the water phase.

In general, OPs were poorly eliminated from the water. In total, only 50% of the OPs in the influent were separated during the treatment process (Table 5). The chlorinated OPs especially tended to pass through the STPs unaffected, while alkyl-OPs were better removed from the water (84–100% of TMP and 35–99% of TBP). Meyer and Bester have reported elimination rates of 55%, 89%, and 75% for TBP, TBEP, and TPP, respectively, and no elimination of chlorinated OPs (18). Previous studies have indicated that chlorinated OPs are more resistant to degradation than alkyl- and aryl-OPs (7, 9, 20). Considering the relatively long retention time of sludge in STPs, alkyl-OPs should be degraded to a large extent. However, the alkyl-OPs TBEP and TBP are still found at

relatively high amounts in sludge (Table 4). This might be explained by the high loads of these compounds that the STPs receive (Table 3 and Figure 2b,c).

The sludge collected at STP 5 had been stored outdoors for 4–6 months (in summertime). Considering the similarities between STPs 1 and 5, regarding their size and the concentrations of OPs in their influent, it is interesting to note that the concentrations of OPs were slightly higher in the sludge from STP 5 than in the sludge from STP 1, even though it had been stored for almost half a year. As we do not know the original concentrations in the sludge from STP 5, we cannot draw any definite conclusions about the degradation of OPs in it, but it seems safe to say that OPs may withstand long periods of storage.

**Mass Balance Estimation.** According to the Swedish water trade association “Svenskt vatten”, Swedish STPs annually treat 1.5 km<sup>3</sup> of wastewater and produce 240 000 tons of sludge (dry weight). This information was used, together with the mean and median values of the concentrations of individual OPs found in the influents, effluents, and sludge in this study, to estimate their average degrees of degradation and environmental load (Table 5). Of the total amount of OPs (54 tons) reaching Swedish STPs annually, 50% (27 tons) is emitted with the effluents and only 1% (0.5 ton) ends up in the sludge. The results indicate that most of the total amount of OPs removed from the water during the treatment processes in the STPs is degraded. The main paths for degradation of OPs in STPs are probably microbial and chemical hydrolysis of the ester bonds, with di- and mo-

noesters and alcohols as products. Further, the total estimated amount of OPs in the influents represents approximately 15% of the registered use (3), which does not include OPs incorporated in imported consumer products. The proportions of the amounts of individual OPs used that can be accounted for vary widely, and are highest for TBP and TBEP (38–52% and 17–22%, respectively), and lowest for TCPP, TDCPP, and TPP (1–5%).

#### Possible Biological Effects of OPs in the Environment.

The levels of the most abundant OPs in the effluents appear to be 3 orders of magnitude lower than their documented 96 h LC<sub>50</sub> values for rainbow trout and fathead minnow (7, 9, 11). Nevertheless, information about the effects of long-term exposure to OPs is scarce, and the possibility that prolonged exposure to lower concentrations of OPs may cause adverse effects in aqueous organisms cannot be excluded. Also, even though most OPs have short to moderate half-lives (days to weeks) and are not considered to be persistent in the environment, their degradation is almost certainly slower in cold climates. Consequently, the risks posed by low concentrations in recipient ecosystems, such as small lakes or streams with low flow rates, and the probability of finding affected organisms may be greater in areas with cold climates than in countries with warmer climates.

In summary, few significant differences in the OP profiles were detected; both the total and individual concentrations of OPs in the influents, effluents, and sludge were quite similar among the studied STPs, indicating that their sources were predominantly diffuse, e.g., products containing flame retardants in general use. Thus, the size of the STP, expressed in terms of personal equivalents, seems to be of minor importance for the OP concentrations. The primary function of STPs is to clean wastewater in order to protect receiving waters and the associated ecosystems from being affected by harmful substances. This study shows, however, that there is little or no removal of chlorinated OPs during the treatment process and overall removal of the OPs studied amounted to only 50%. Consequently, about 27 tons of total OPs is annually emitted to recipients outside Swedish STPs.

There is a need for further studies on the potential biological effects of OPs in wastewater recipients, preferably performed in springtime, which is likely to be the most critical time for aqueous organisms when they are in vulnerable stages of their life cycles, such as eggs and larvae.

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#### Literature Cited

- (1) SRI Consulting. Consumption of flame retardants. <http://www.cefic-efra.com/content/Default.asp?PageID=7>, 2004 (accessed May 27, 2005).

- (2) Westrop, N. [EFRA (European Flame Retardant Association)], personal communication, 2004.
- (3) KemI. *The Products Register*; National Chemical Inspectorate of Sweden: Sundbyberg, Sweden, 2004.
- (4) European Commission. *Regulation (EC) No. 2268/95 of 27 September 1995 concerning the second list of priority substances as foreseen under Council Regulation (EEC) No. 793/3*; European Chemicals Bureau: Ispra, Italy, 1995.
- (5) European Commission. *Regulation (EC) No. 2364/2000 of 25 October 2000 concerning the fourth list of priority substances as foreseen under Council Regulation (EEC) No. 793/3*; European Chemicals Bureau: Ispra, Italy, 2000.
- (6) *IUCLID International Uniform Chemical Information Database*, 2nd ed. [CD-ROM]; European Chemicals Bureau: Ispra, Italy, 2000.
- (7) World Health Organization. *Flame Retardants: Tris(chloropropyl) Phosphate and Tris(2-chloroethyl) Phosphate*; Environmental Health Criteria 209; Geneva, Switzerland, 1998.
- (8) Agency for Toxic Substances and Disease Registry. *Toxicological profile for hydraulic fluids*; U.S. Department of Health and Human Services: Atlanta, GA, 1997.
- (9) World Health Organization. *Tributyl Phosphate*; Environmental Health Criteria 112; Geneva, Switzerland, 1991.
- (10) Lanxess Energizing Chemistry. *Antifoam T. Product Description*; Lanxess Deutschland GmbH: Leverkusen, Germany, 2004; [http://phosphor-chemikalien.de/P/download/Phosphorchemikalien\\_e/Antifoam\\_T\\_e.pdf](http://phosphor-chemikalien.de/P/download/Phosphorchemikalien_e/Antifoam_T_e.pdf) (accessed Feb 7, 2005).
- (11) World Health Organization. *Flame Retardants: Tris(2-butoxyethyl) Phosphate, Tris(2-ethylhexyl) Phosphate and Tetrakis(hydroxymethyl) Phosphonium Salts*; Environmental Health Criteria 218; Geneva, Switzerland, 2000.
- (12) Wensing, M.; Uhde, E.; Salthammer, T. Plastics additives in the indoor environment—flame retardants and plasticizers. *Sci. Total Environ.* **2005**, *339*, 19–40.
- (13) Fries, E.; Püttmann, W. Monitoring of the three organophosphate esters TBP, TCEP and TBEP in river water and ground water (Oder, Germany). *J. Environ. Monit.* **2003**, *5*, 346–352.
- (14) Marklund, A.; Andersson, B.; Haglund, P. Traffic as a source of organophosphorus flame retardants and plasticizers in snow. *Environ. Sci. Technol.* **2005**, *39*, 3555–3562.
- (15) Paxeus, N.; Robinson, P.; Balmer, P. Study of Organic Pollutants in Municipal Waste-Water in Göteborg, Sweden. *Water Sci. Technol.* **1992**, *25*, 249–256.
- (16) Paxeus, N. Organic pollutants in the effluents of large wastewater treatment plants in Sweden. *Water Res.* **1996**, *30*, 1115–1122.
- (17) Andresen, J. A.; Grundmann, A.; Bester, K. Organophosphorus flame retardants and plasticizers in surface waters. *Sci. Total Environ.* **2004**, *332*, 155–166.
- (18) Meyer, J.; Bester, K. Organophosphate flame retardants and plasticizers in wastewater treatment plants. *J. Environ. Monit.* **2004**, *6*, 599–605.
- (19) Fries, E.; Püttmann, W. Occurrence of organophosphate esters in surface water and ground water in Germany. *J. Environ. Monit.* **2001**, *3*, 621–626.
- (20) World Health Organization. *Triphenyl Phosphate*; Environmental Health Criteria 111; Geneva, Switzerland, 1991.
- (21) Bester, K. Comparison of TCPP concentrations in sludge and wastewater in a typical German sewage treatment plant—comparison of sewage sludge from 20 plants. *J. Environ. Monit.* **2005**, *7*, 509–513.
- (22) Marklund, A.; Andersson, B.; Haglund, P. Screening of organophosphorus compounds and their distribution in various indoor environments. *Chemosphere* **2003**, *53*, 1137–1146.

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