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The Role of Detergents in the Phosphate-Balance of European Surface Waters

ABSTRACT

This paper provides a generic overview of a source-apportionment for phosphorus (P) in surface waters of 18 European countries by showing the relative significance of each source in the environment. The major identified P-inputs are from municipal sewage water (human wastes and detergents), industry and from diffuse and natural sources, respectively. Focus in this study is given to P from laundry and automatic dishwashing detergents (ADD). P from municipal wastewater is been reduced significantly in countries with a high degree of connectivity to sewage treatment facilities. However, P from detergents may still account for up to 28% in surface waters of countries, where sewage treatment is poor and P-containing laundry detergents are dominant. In countries where the market share of P-free laundry detergents is already 100% the remaining P from ADD has relatively little impact on the total P in surface waters. Hence especially in eutrophication sensitive areas, where efficient P removal from sewages is regulated by the Urban Waste Water Treatment Directive (91/271/EEC), P from ADD may not significantly contribute to their nutrient status (1-6%). In the context of the new EU-Detergent Regulation (648/2004/EEC) requiring the EU-Commission to evaluate the use of P in detergents, a limitation or ban of P in the product category of ADD seems inadequate.

1. INTRODUCTION

Phosphorus (P) is one of the main limiting factors for biomass production in nature and P-emissions have been recognised (beside nitrogen) to be a major contributor to eutrophication in the aquatic environment. During the past decades actions to reduce the loads of P in surface waters were taken by several countries including the USA, Japan and some EU member states. In the EU these actions included the implementation of voluntary agreements to reduce the use of P-based detergents but also an improved waste water treatment by implementation of the Urban Waste water Treatment Directive (UWWTD: Directive 91/271/EEC). The latter requires a tertiary P-elimination step for all municipal sewage treatment plants (STP) of agglomerations of >10,000 population equivalents (p.e.) in areas sensitive to eutrophication.

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As the major P-sources to surface waters, diffuse non-point sources (e.g. agricultural runoff or erosion, animal husbandry and groundwater via leaching from soils), point sources such as municipal and industrial waste water discharges were identified [1]-[3]. Although the relative importance of these sources may vary on the regional and local scale, a source balance on the country level can provide a good general overview of its relative contributions. This paper reports on the current status of the major sources of P into the aquatic environment in 18 EU member states. Emphasis is given to the P inputs from laundry and automatic dishwashing detergents (ADD) analysing the relative environmental relevance of these applications for the individual country.

Laundry and dishwashing detergents consist of a variety of compounds of which surfactants, builders and bleaching systems are the major ingredient groups. Sodium tri-Polyphosphates (STPP) have been used for a long time as builders in heavy duty laundry detergents to provide optimum washing conditions (e.g. reduction of water hardness, stabilisation of alkalinity) and also to stabilise the powder grains in a formulated detergent product (STTP content typically 20-50%, depending on detergent type). Liquid detergents do not contain STPP-based builder systems. As a consequence of P-reduction measures, STPP has been successfully replaced by zeolites and alternative builders in many countries. In contrast, ADD are still P-based because of the unbeatable anti-scaling effects of STPP. This holds true for all main brands in all countries in the world. ADD contain typical concentrations of approximately 50% STPP. Contrary to laundry detergents, STPP substitutes cannot be used in ADD, as they are either insoluble or are not considered to offer adequate cleaning performance (e.g. citrates or polycarboxylates [4]). Therefore, the relative contribution of P from ADD in the environment is an important issue in the context of the EU-Detergent Regulation (EEC 648/2004), which requires the EU-commission to evaluate possible P-limitations by April 2007.

2. VOLUMES AND USE OF PHOSPHATES

The commercial market for phosphoric acid and its salts is broadly subdivided into agricultural and industrial categories. Agricultural end uses include P-containing chemicals in fertilizers and livestock feed supplements. All other uses are considered industrial, including: Detergent builders, Water treatment, Food and beverage additives, etc. [5]

The worldwide consumption of P in 2001 was 39.5 million t P_2O_5 [6]. The main user of P is the fertiliser industry; its total world consumption is estimated to be 33.4 million t/a in 2002/2003 [7], i.e. ca 85%. For Europe, a consumption of 3.6 million t P_2O_5 was reported for the same time period. Only approximately 1/10 (529 000 t P_2O_5) of the total P-volume is used mainly in the food and detergent industries [8]. In Western Europe the use of P in detergents still accounts for the main fraction of industrial P use (61%, 313 000t/a) followed by diverse institutional and industrial applications (30%) and the use in food and beverage industries (9%) ([5] Fig. 1). Among the domestic detergent applications approximately 27% STPP per annum can be attributed to ADD applications in Europe (mainly western EU).
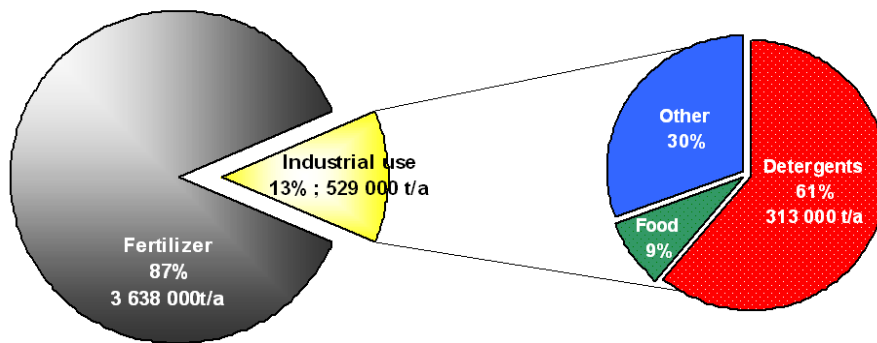
Figure 1: Use and distribution of Phosphates (as P₂O₅) in Western Europe
(* „Other" includes I&I applications)

2.1. SOURCES OF P IN THE ENVIRONMENT

The P-load of surface waters results from non-point sources such as agricultural runoff or erosion and animal husbandry, and from point source municipal and industrial waste water discharges. Further diffusive sources were identified which may enter via atmospheric deposition and groundwater [1],[3]. The relative importance of these sources varies widely between countries and regional catchments, depending e.g. on the degree of urbanisation, the standard of sewage treatment and the nature and intensity of agricultural practices. While industrial sources may be important locally, the two major widespread sources of P into surface water are diffuse agriculture inputs and municipal wastewater. The main sources of P in surface waters that were analysed in detail in this paper are depicted schematically in Fig 2.
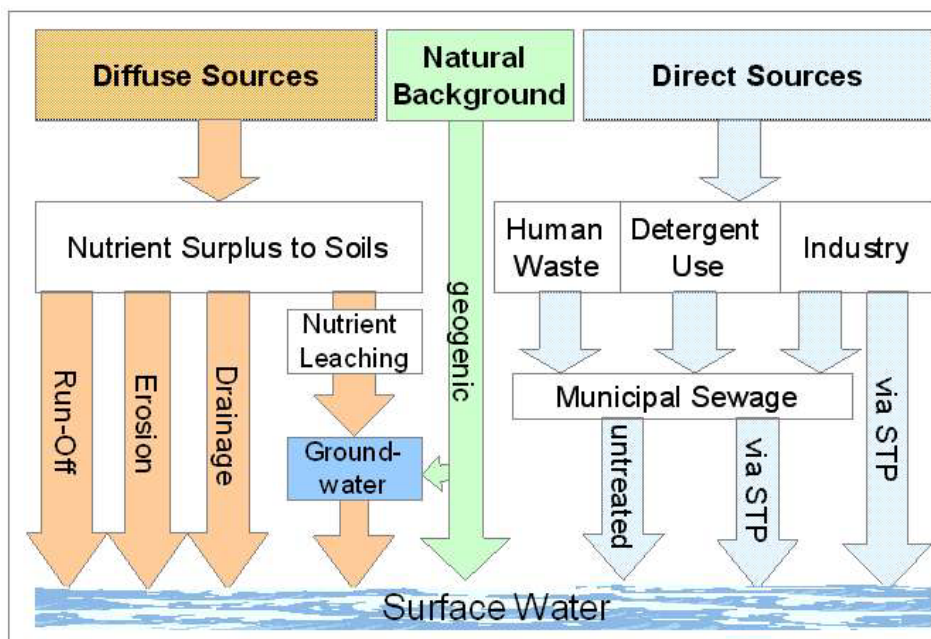

Figure 2 : Schematic picture of the P-source apportionment. Main quantified sources are diffusive source, natural background, human wastes, P from detergent use and industry emissions.

According to data from 16 EU-member states, the total emissions of P to the environment in Europe decreased in sum by approximately 20% between 1999 to 2003 [9]. This development, which is mainly due to the reduction of fertilizer consumption is reflected by statistics of the International Fertilizer Industry Association for Western Europe [7]. This trend may continue in the near future. As it is the aim of this paper to provide a current status of the major sources of P into the aquatic environment it has to be taken into account that this work considered data, which may be - although the most recent - up to 3-7 years old due to the characteristics of gathering and reporting.

2.1.1. WASTE WATER

The majority of P enters natural waters in a non-bioavailable form, bound to particulate matter (e.g. from runoff, erosion), while only around 5% occur in soluble form. However, soluble P in sewage effluent amounts for up to 90% of the total P-content in highly impacted catchments but typically may account for around 70% [10],[11]. Main sources of P in municipal waste water are P-containing detergents and human faeces, urine etc. and – in general terms - additional discharges from small industries and institutional activities described as population equivalents (p.e.).

- DETERGENTS

Detergent P (as STPP) released with the laundry waste water are quickly hydrolysed to ortho-phosphate. Thus, where STPP is used as builder in laundry detergents (e.g. in many of the new EU-member states), it is estimated to contribute between 25-50% of soluble (bioavailable) P in untreated municipal wastewaters [8],[12],[13]. Household washing and cleaning agents are divided into several types like laundry detergents, softeners, multi-purpose cleaners, dishwashing agents, etc. According to market share data [14], approximately 66% of the total household detergent use in Europe can be attributed to laundry detergents (incl. softeners) and additives while 16% are hand dishwashing detergents and ADD (Table 1). Specific data for Germany [15] roughly support these estimates (64% household; 18% ADD). In households, P is used mainly in detergents (laundry and ADD) and to a less extent in special cleaning products (e.g. for car care).

Table 1 : Estimated annual consumption of household detergents in Europe
(Henkel, internal market data)

Product	Annual consumption (2005)	
	Europe (tons)	% of total
Heavy Duty Laundry detergents (powders & liquids)	4 440 000	45%
Fabric softeners	1 540 000	16%
All-purpose cleaning agents	1 470 000	15%
Hand dishwashing agents	1 000 000	10%
Laundry Additives	717 350	5%
Machine dishwashing agents	528 000*	6%
Toilet cleaning agents	252 000	3%

*only ca. 48% of this tonnage refers to P-containing cleaners, the remaining tonnage is related to salt, rinser, etc.

P-emissions from detergents are calculated from market volume and/or per capita use of detergents of the different countries. These numbers may differ significantly in literature for a single country [8],[16],[17]. For the present study, data for laundry detergent usage were taken from AISE [16] as these numbers rather show higher consumption figures and therefore represent a worst case situation in terms of the P-contribution of detergents. The use habits of laundry detergents are quite different even within Western European countries showing variations up to a factor of 3. Fig. 3 shows data for EU-15 but also the consumption figures of three countries that joined the EU recently (EU-18). While consumption of laundry detergents in Western Europe ranges between 4.2 and 11.7 kg/cap/a [16], the consumption in Central and Eastern Europe varies between 2.0 kg/cap/a (Ukraine) and 10 kg/cap/a (Slovenia) (Henkel, internal data). The total weighted mean of laundry detergent use in the EU-18 is at 8.7 kg/cap/a. According to market data (Henkel, internal data), the ADD consumption as reported by Glennie et al. [8] needs to be specified to the cleaner fraction of the product category "ADD" to allow a reasonable P-balance, accounting for approximately only 48% of the originally reported values. Thus, ADD cleaner product usage shows 0.1-0.9 kg ADD/cap/a with a total mean of 0.5 kg/cap/a in EU-18 (Fig 3).

Figure 3 : Detergent- and STPP-consumption (from Laundry and Dishwashing) per capita in 18 EU countries in 1998/2004

Market shares of P-containing laundry detergents as reported in the literature for 1998 [17],[18] were used for the estimation of STPP- and P-tonnages for this product category. Hence, some uncertainties may result if the current market shares had changed. In fact, AISE recently released data from an internal survey indicating a further decrease of P-containing laundry detergents in several countries. Nevertheless, the reported data from 1998 provide a good starting point for a conservative estimation of the relative P-contribution of detergents in surface waters.

While STPP-based conventional laundry detergent powders contain 20-25% STPP, compact powders and tablets may contain up to 50% STPP; P-containing builders are not used in liquid detergents. According to the data available for several countries [18] a mean market share of 49% for conventional powders and 39% compact powders and tablets was calculated for the EU. In countries lacking specific data these market shares were used to calculate STPP from laundry detergent consumption figures. In the remaining countries the specific reported market distributions were taken directly as the basis for STPP-tonnage estimations. A mean content of 50% STPP was assumed for ADD. The total P-tonnage from detergents can be derived from STPP in detergents and calculated for individual countries (cf. Fig 3, white bar) according to:

$$STPP_{tonnage} = STPP(Laundry\ Detergent) + STPP(ADD)$$

$$= (V_{LD/cap} \times cap \times \%_{STPP\ use/country} \times \%_{STPP\ in\ detergent}) + (V_{ADD/cap} \times cap \times \%_{STPP\ in\ detergent})$$

where:

$V_{LD/cap}$ = the total laundry detergent product volume in tonnes per year

$V_{ADD/cap}$ = the total ADD product volume in tonnes per year

$\%STPP_{use/country}$ = the country specific marked share of P-based detergents

$\%STPP_{in\ detergent}$ = the fraction of STPP in detergents

cap = capita

$V_{LD/cap}$ is calculated separately for both fractions, conventional and compact powder, as the content of these detergent types significantly differs (see above). Based on the calculated STPP volumes it can be seen that STPP from ADD accounts for 27% of the total detergent-based STPP emissions in the average. A weighted mean consumption of 0.9 kg STPP/cap/a in EU-18 (Fig 3) can be calculated which varies between 0.1-2.5 kg STPP/cap/a for individual countries. In order to calculate from STPP to P the conversion factor of 0.2527 is applied (Table 2).

Table 2 :   *Population size in EU-18, per capita use of laundry detergents and ADD, and resulting annual product tonnages. Corresponding P volumes (converted to P) and fraction of P in detergents according to individual market situation by country*

Country	Pop. (2000)	Detergent consumption					P from Detergent	
		Laundry			ADD			
		Det. with STPP	Con-sump.[1]	Volume	Con-sump.	Volume	Volume	P from ADD
	x 1000 cap	%	kg/cap/a	x1000 t/a	kg/cap/a	x1000 t/a	x1000 t P/a	%
Austria	8102	0	6.9	56	0.8	6.5	0.82	100%
Belgium-Luxembourg	10686	0	9.7	103	0.7	7.2	0.91	100%
Denmark	5322	20	5.2	28	0.9	4.8	1.04	59%
Finland	5177	10	4.2	22	0.6	3.4	0.59	71%
France	59296	50	9.9	584	0.6	36	22.13	21%
Germany	82282	0	7.7	632	0.7	56	7.10	100%
Greece	10903	50	9.8	107	0.4	4.3	4.65	12%
Ireland	3819	0	9.0	34	0.4	1.4	0.18	100%
Italy	57536	0	11.7	671	0.4	26	1.48	100%
Netherlands	15898	0	7.3	115	0.6	10	1.27	100%
Portugal	10016	70	11.3	113	0.1	0.9	6.23	2%
Spain	40752	60	11.4	465	0.3	12	17.24	9%
Sweden	8856	15	4.5	40	0.5	4.3	1.01	54%
United Kingdom	58907	45	8.3	488	0.7	41	22.09	23%
Czech Rep	10269	65	7.0[2]	26	0.3	2.8	2.10	17%
Hungary	10012	70	8.4[2]	84	0.1	1.1	2.22	7%
Poland	38671	85	4.8[2]	186	0.1	2.6	6.73	5%
Total (rounded)	436504	31[3]	8.7[3]	4200	0.5	214	98	27%

[1] IBM 2002

[2] Henkel, internal data, 2004

[3] weighted mean

- HUMAN WASTES AND POPULATION EQUIVALENTS

Roughly 1.6 g of P per capita and day is assumed to be contributed from human urine and feces into the sewage [[11],[12],[19]]. The total P-load from this source can be calculated by considering the number of inhabitants of each country [20]. An additional P-load to sewage water originates from small industries (e.g. nutrient industries) and institutional uses of P-containing products. This fraction is extremely difficult to quantify but must be considered in order to relate the real wastewater load to a number of population equivalents (p.e.). It has been assumed that this fraction corresponds to approximately 40% of the household freight in raw sewages [21].

2.1.2. DIFFUSE SOURCES

The P-contribution of nonpoint-source pollution by leaching, erosion and runoff from soils is very important (diffuse sources, Fig. 4). A major source of P in surface water originates from agricultural areas. It is notable that in countries with high animal manure production, application of mineral fertilizers per ha is rather higher than lower. The national estimates have been related to national statistics on fertilizer consumption such as the Food and Agriculture Organisation's (FAO) data [22]. The European Environmental Agency [3] indicated a clear relationship between total fertilizer consumption and diffuse agricultural losses in the country scale, while this may differ on regional scale depending on hydrological and geological specifications. Thus, P-loss is higher especially in those areas with intensive livestock production systems.
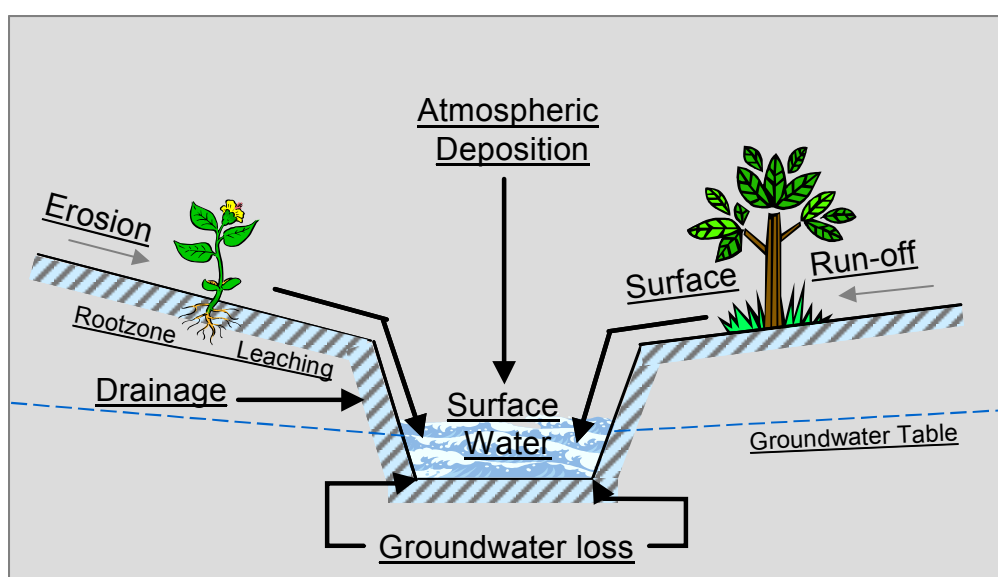

Figure 4 : The most important 'hydrological' pathways with regard to P losses from diffuse sources to aquatic systems

While fertilizer consumption in Western Europe continuously decreased during the past decades [7] it has to be considered, that despite this downward trend, there will still be a continuous net increase of P-input into surface waters for a long time due to the geo-accumulation of P in European soils [23]. Today, many of the European soils have higher P-contents than can be used by crops, hence, maintaining the risk of P-losses over time. In the EU-18, the average P-application is 4-11 kg P/ha/a (mean 6 kg P/ha/a) from artificial fertilizer and 4-60 kg P/ha/a from manure (mean 15 kg P/ha/a [24]). Thus, a EU-mean of P applied to arable land of 22 kg P/ha/a can be calculated.

Although P applied as fertilizer is not very soluble, runoff coefficients have been calculated mainly between 0.3-1.0 kg P/ha/a for agricultural land. The European Environmental Agency [3] calculated the total anthropogenic diffusive loss in two river catchments of the Baltic and the North Sea to range between 0.14-0.43 kg P/ha/a, which compares well with the reported range. Estimating P leaching is complicated because the process is influenced by a range of factors including soil and land use type, hydro-geological and climatic conditions. Therefore, to account for differences in P-fertilizer practice of each country generically, for agricultural land, a run-off coefficient at the lower end of the reported range (0.5 kg P/ha/a) has been

assumed for countries with low total P-fertilizer use, while a run-off at the upper end of the range (0.8 kg P/ha/a) has been applied to the arable land area in countries with high total use of fertilizer (i.e. above the EU-mean of 22 kg P/ha/a). The P-balance on arable land indicates that in the EU-18 mean 93% of the applied P will remain on the fields, while only 7% is lost due to run-off (Table 3). In fact, today much of the European soils have higher P-contents as can be used by crops, hence, increasing the risk of P-losses over time due to P-saturation of the soils. Loss rates of P from catchments with natural vegetation (mainly forests) have been reported to be between 0.05-0.1 kg P/ha/a [2],[8]. For the P-balance calculations run-off from non-arable land was assumed to be the mean of the reported range (0.075 kg P/ha/a). The P-emission estimates in this report were considered as run-off from non-arable and agricultural land separately (Table 3).

Table 3 :   Use of fertilizer and animal manure in European countries in 2002 (Source: FAO Stat Data 2005) and corresponding calculated runoff from arable and non-arable land

	Arable Land					Non-Arable Land	
	Land use	Synth. Fertilizer Application		Animal Manure* Application		P-Runoff	Land use	P-Runoff
	1 000 000 ha	(kg P/ha/a)	(in 1000t P/a)	(kg P/ha/a)	(in 1000t P/a)	(in 1000t P/a)	1 000 000 ha	(in 1000t P/a)
Austria	3.5	6	21	10	37	**1.77**	3.3	**0.25**
Belgium-Luxembourg	1.8	11	20	38	68	**1.44**	0.7	**0.05**
Denmark	3.1	5	14	22	67	**2.48**	0.7	**0.05**
Finland	2.9	8	23	8	24	**1.43**	22.7	**1.70**
France	34.9	9	318	9	318	**17.45**	16.6	**1.25**
Germany	18.8	8	143	20	371	**15.07**	11.3	**0.85**
Greece	4.6	10	47	3	13	**2.30**	3.4	**0.25**
Ireland	4.3	10	42	9	39	**2.16**	0.4	**0.03**
Italy	19.3	8	162	10	193	**9.63**	7.5	**0.56**
Netherlands	2.4	10	23	62	146	**1.90**	0.4	**0.03**
Portugal	4.8	5	25	6	27	**2.40**	4.0	**0.30**
Spain	29.8	9	262	4	125	**14.91**	20.2	**1.52**
Sweden	4.1	4	117	8	35	**2.06**	23.8	**1.78**
United Kingdom	17.7	7	123	9	161	**8.87**	2.4	**0.18**
Czech Rep.	4.1	5	21	12	48	**2.07**	2.7	**0.20**
Hungary	6.1	5	30	9	52	**3.04**	1.9	**0.14**
Poland	17.1	8	132	8	140	**8.55**	10.5	**0.79**
EU-18	180	7	1523	14	1863	**97.5**	189	**9.9**

* Source adapted from Sibbersen and Metzger (1995)

As P is retained to a great extent in the soil further diffusive fluxes via the groundwater can become significant. However, exact modelling of this P-input into surface waters appear to be rather complex, because variable soil characteristics, local precipitation and groundwater fluxes may highly influence the retention properties of P in this compartment. Groundwater concentrations of P in agricultural soils in Germany have been reported to be in the range of 0,03-0,1 mg/l [1]. For Germany the authors calculated the diffusive P-input from groundwater

to account for ca 17% of the total P-load into surface waters. Further calculations based on modelling with MONERIS in river catchments of 11 European countries showed very variable but generally significant P-fractions of 0,7-42% (mean 17%) that could be attributed to groundwater [25]. In the absence of specific data for groundwater input of P in the different countries, the lower 10th-percentile of the groundwater P-fractions from of the above mentioned European catchments was assumed as a minimum default input for this diffusive entry path. Thus 5% of total P load (except for Germany: 17%) was added by default. As mentioned this conservative estimation implies high uncertainties as the real input could be well above this fraction.

Emissions from groundwater plus the emissions via run-off are considered as total diffusive sources in further P-balancing calculations. Comparison with in-depth analyses for Germany [1] showed, that this procedure covers total diffusive sources sufficiently.

2.1.3. INDUSTRY

Except for a few countries industrial point sources do not contribute significantly to P emissions in EU countries. OSPAR [26] estimated a reduction of P-emission from industrial plants from 1985 to 2000 in the range of 25-99%. Total estimated loads of industry in OSPAR countries are depicted in Table 4. While in some countries industrial point sources represent a significant fraction of the total P-loads (e.g. Netherlands 38%), in most countries industrial P-sources are of minor importance. In Germany the 10 main industrial point sources in the year 2001 accounted for approximately only 300 t P/a [27], corresponding to less than 2% of the total anthropogenic input.

Table 4 : Discharges of P (1000t/a) not connected to municipal sewage systems (OSPAR 2003)

	P-1985	P-2000	Reduction	Per-capita industrial load [g/cap/a]
Belgium	5.460	0.797	85%	75
Denmark	3.100	0.038	99%	9
Germany	6.146	1.104*	82%	13
Netherlands	13.422	1.755	87%	110
Norway	0.164	0.102	38%	22
Sweden	0.118	0.088	25%	58
Switzerland	0.153	0.020	87%	3

* reported emissions for 2001: 300t/a (UBA, 2001)

Because industrial input is sparsely reported in literature [26],[28], estimations of industrial sources in this study were based on a per capita-specific calculation of industrial P-emissions per country, based on the numbers shown in Table 4. This specific value ranged from 3 g/cap/a (Switzerland) to 110g/cap/a (Netherlands). For the approximation of countries without reported P-emissions from industry the median of 25 g/cap/a was used.

2.1.4. NATURAL BACKGROUND

The European Environmental Agency [29] reports a decline of the orthophosphate concentrations in rivers of the EU-15 countries and new EU member states (accession states) in the 1990's reflecting the general improvement in waste water treatment and the replacement of STPP by zeolites in laundry detergents over the period 1990 –2000. Natural concentrations of orthophosphate vary from catchment to catchment depending upon factors such as geology and soil type. Natural ranges are considered to be approximately between <0.1 to 10 µg P/l. Therefore, a mean of 5 µg/l has been assumed as geogenic to calculate the P-tonnage of natural background by multiplying with the total water volume, internally produced in each country [22].

3. P-REDUCTION IN SEWAGE TREATMENT

An important factor to reduce P from waste water is the sewage treatment process allowing removal of P efficiently up to more than 90% if modern tertiary treatment (including P-precipitation) is applied (Table 5).

Table 5 : Total treatment efficiency (P-removal) in sewage treatment containing... (Folke 1996)

…primary treatment	5-15%
…secondary treatment	10-40%
…tertiary treatment	>90%

In many countries only a part of the population is connected to municipal sewage treatment plants. However, EUROSTAT [20] claims that 90% of the EU-25 population has been connected to sewage systems today and the degree of population connected to public sewage treatment plants is roughly 80% by mean (Fig 5).
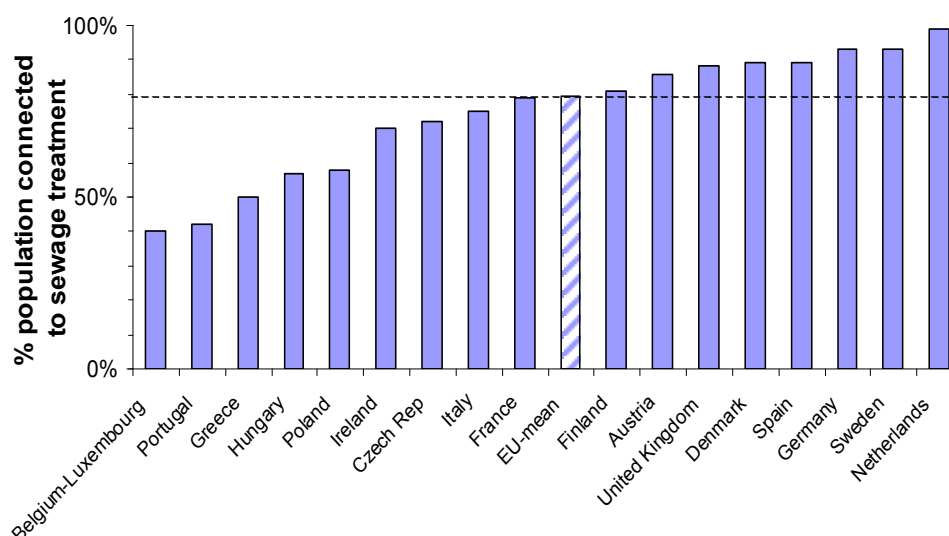

Figure 5 : Population connected to municipal sewage treatment plants (STP); (Eurostat 2006)

According to the current connectivity of the population in different countries, a part of the raw sewage remains untreated. However, for the P-balance in surface waters this part can usually not considered as completely untreated because an increasing part of the population which is not connected to sewage systems treat their sewage before its release into the environment e.g. by decentralised sewage treatment plants. Another part is percolated in soils and thus may contribute to diffuse P-sources, while a third fraction may be released directly into surface waters. To account for these different entry pathways the current calculation assumes a P-reduction of 30% by default of the "untreated fraction" of raw sewage, which is comparable to an efficiency estimate of small decentralised STPs in Germany [11].

4. BALANCE OF EMISSION VOLUMES

4.1. GROSS SOURCE APPORTIONMENT

This chapter takes account of the emission volumes calculated previously (Tables 2 and 3) and provides a complete source apportionment of P in the different countries. It is obvious that man-made P-emissions from household products account for a significant amount of P entering to the environment (Table 6, Figure 6). The P contribution from detergents in the raw sewage ranges between 3% (Italy) to 43% (Portugal). These variations mainly result from the different country-specific measures for the P-restriction in laundry detergents.

Table 6 :   Gross P balance from different sources based on untreated sewage input

Country	population	Natural/ Diffusive Sources		Direct Sources			Total
		Natural Back-ground	Diffusive sources**	Industrial sources	P from Detergent	P from human faeces and waste	
	(in 2000)					Raw sewage	
	x 1000			[x1000 t P/a]			
Austria*	8102	0.28	2.22	0.20	0.82	6.95	10.5
Belgium-Luxembourg*	10686	0.07	1.84	0.80	0.91	9.10	12.7
Denmark	5322	0.02	2.71	0.05	1.04	4.59	8.4
Finland	5177	0.53	3.39	0.37	0.59	4.40	9.3
France	59296	0.88	20.57	1.48	22.13	50.32	95.4
Germany*	82282	0.53	20.77	1.10	7.10	70.11	99.6
Greece	10903	0.28	2.98	0.27	4.65	9.13	17.3
Ireland*	3819	0.24	2.36	0.10	0.18	3.20	6.1
Italy*	57536	0.85	11.43	1.44	1.48	47.63	62.8
Netherlands*	15898	0.06	2.19	1.76	1.27	13.51	18.8
Portugal	10016	0.19	3.18	0.25	6.23	8.24	18.1
Spain	40752	0.55	17.75	1.02	17.24	33.93	70.5
Sweden	8856	0.85	4.17	0.52	1.01	7.46	14.1
United Kingdom	58907	0.72	10.24	1.47	22.09	50.22	84.7
Czech Rep	10269	0.07	2.55	0.26	2.10	8.54	13.5
Hungary	10012	0.03	3.54	0.25	2.22	8.24	14.3
Poland	38671	0.27	10.55	1.07	6.73	31.75	50.3
EU-18	436504	6.40	122.43	12.51	97.81	367.33	606.5

* Countries in which STPP from laundry detergents have been replaced by 100%
** Diffusive sources correspond to run-off from arable- & non-arable land and groundwater
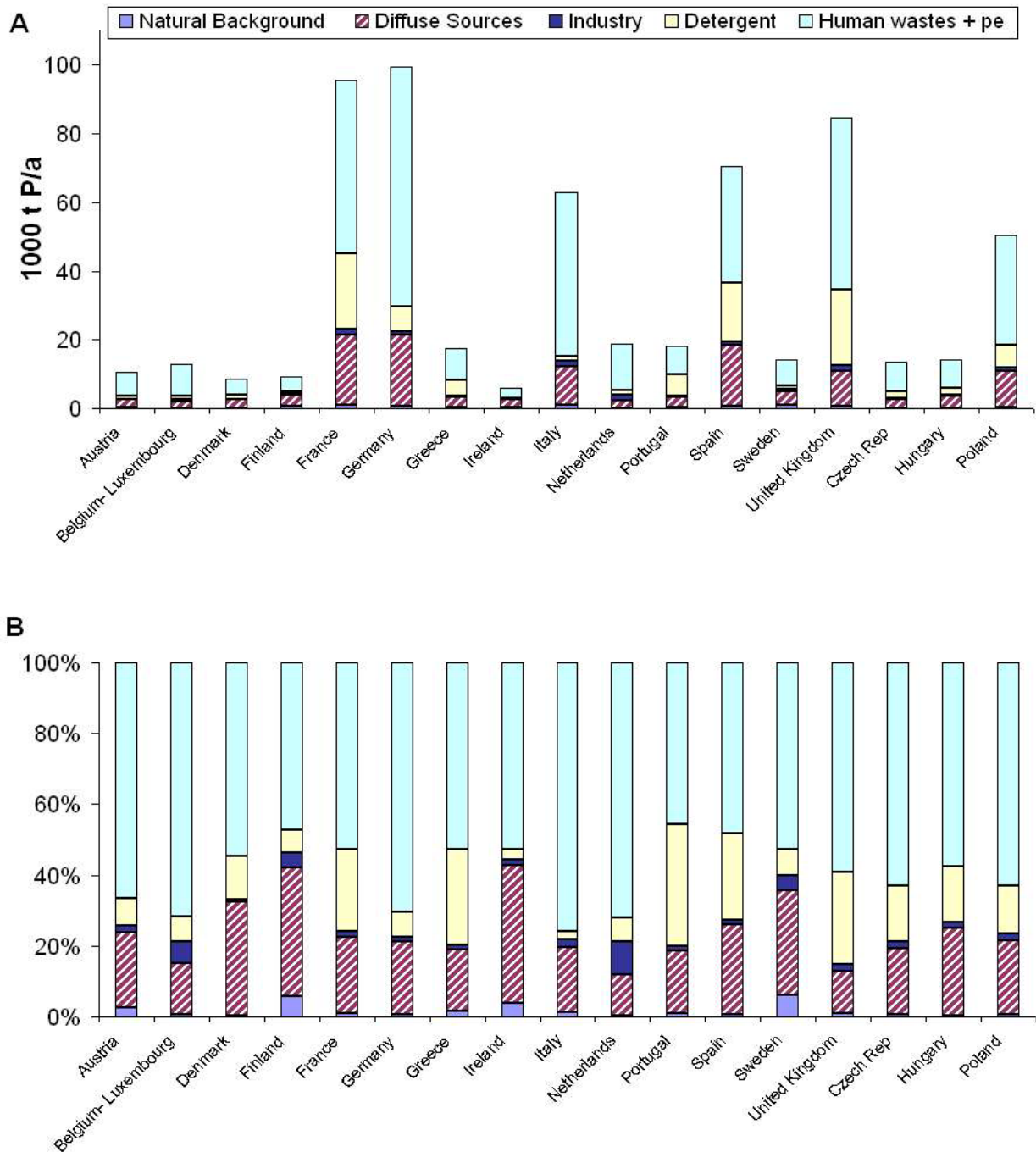
Figure 6 : P-source apportionment for EU-18 countries. A: Total tonnage in 1000t/a; B: Fractions in %. Note: no sewage treatment is considered for the calculation of P from human wastes and detergents (gross inputs)

From Table 6 and Figure 6A, a picture of total P-loads (in 1000 tonnes P per year) coming from different sources can be obtained. However, the absolute figures are not useful for comparison between countries because they depend on catchment and population size. Therefore, the relative fractions of individual P-sources are shown in Fig 6B. The comparison of these fractions with the total P entering surface waters allows to assess the impact of

detergents. Note that no sewage treatment has been assumed for these numbers (=gross inputs). It can be seen that P from waste water (human wastes and detergents) contribute to roughly 50-80% of the gross release of P. The high contribution of P entering waste waters emphasise the demand for effective waste water treatment especially in densely populated countries.

4.2. THE ROLE OF DETERGENTS IN SURFACE WATER

As shown above, the degree of the population connected to sewage treatment is different for individual countries. Additionally, consistent data on the distribution of different types of sewage treatment plants do not exist for each country. Table 7 provides a summary of the P-fractions from sewages (human wastes and detergents) into surface waters, resulting from different scenarios that account for untreated ('gross input') and treated sewage (secondary treatment = 'Scenario 1' and tertiary = 'Scenario 2') considering STP-connectivity data as shown in Fig 5 [20]. The fraction of P originating from detergents that goes into surface waters will be depicted as 'P-Det' in the following. In general the contribution of P from municipal sewages and consequently from detergents decreases dramatically due to sewage treatment. Hence, when assuming only secondary treatment an overall P-reduction of up to 33% in surface waters is calculated, while up to 71% P-reduction is calculated if tertiary treatment is established. The latter high reduction is achieved when STP connectivity is high (e.g. in the Netherlands and Sweden). It can be assumed that the real sewage treatment situation in each country is a result of individual compositions of the two depicted sewage treatment scenarios. Therefore, the real fractions must be assumed to be within a given range. Maximum P-Det of 28-31% is seen in countries were P-free detergents are not widely used and the sewage treatment situation is bad as well (e.g. in Portugal). In countries with low connectivity of the population to sewage treatment the differences of P-Det between secondary treatment and tertiary treatment decreases (e.g. Belgium). On the other hand, the higher the market share of P-free laundry detergents the lower is P-Det (cf. data in Table 2). In some countries P-Det is rather small (e.g. in Italy, Ireland and Germany). In these countries two factors come into play: first STP connectivity is above the EU-mean of 80% and secondly P-based laundry detergents have been replaced on the marked. It can be assumed that these two factors play an important role in determining P-Det in the future [30].

Table 7 :   P-fractions from sewage (detergents and human wastes) into surface water considering no treatment (gross loadings) or secondary (Scenario 1)- and tertiary (Scenario 2) treatment, respectively. Note: sewage from population not connected to STP received 30% P-reduction by default (see text for details). STP connection according Eurostat (2006)

	Population connected to STP	Gross input no Sewage Treatment			Scenario 1 Secondary Treatment			Scenario 2 Tertiary Treatment		
		P-Det	Human wastes	Sum	P-Det	Human wastes	Sum	P-Det	Human wastes	Sum
Austria	86%	8%	66%	74%	**7%**	57%	64%	**4%**	31%	35%
Belgium-Luxembourg	40%	7%	72%	79%	**6%**	65%	71%	**6%**	57%	63%
Denmark	89%	12%	55%	67%	**10%**	45%	55%	**5%**	21%	26%
Finland	81%	6%	47%	53%	**5%**	37%	42%	**2%**	17%	20%
France	79%	23%	53%	76%	**20%**	46%	66%	**13%**	29%	42%
Germany	93%	7%	70%	77%	**6%**	61%	67%	**3%**	30%	33%
Greece	50%	27%	53%	80%	**24%**	48%	72%	**21%**	40%	61%
Ireland	70%	3%	53%	56%	**2%**	42%	44%	**1%**	25%	26%
Italy	75%	2%	76%	78%	**2%**	67%	69%	**1%**	46%	47%
Netherlands	99%	7%	72%	79%	**6%**	63%	69%	**2%**	26%	28%
Portugal	42%	34%	46%	80%	**31%**	41%	72%	**28%**	37%	65%
Spain	89%	24%	48%	72%	**21%**	41%	62%	**10%**	20%	30%
Sweden	93%	7%	53%	60%	**6%**	42%	48%	**2%**	15%	17%
United Kingdom	88%	26%	59%	85%	**24%**	54%	78%	**15%**	35%	50%
Czech Rep	72%	16%	63%	79%	**14%**	56%	70%	**10%**	40%	50%
Hungary	57%	16%	58%	74%	**14%**	50%	64%	**11%**	39%	50%
Poland	58%	13%	63%	76%	**12%**	56%	68%	**9%**	44%	53%
EU-18 mean	80%	15%	61%	76%	**13%**	53%	66%	**8%**	33%	41%

The relative impact of ADD-P to P-Det ($P\text{-}Det_{ADD}$) can be evaluated in countries where only P-free laundry detergents are on the market (e.g. Germany, Belgium, Austria). It can be seen, that the impact of ADD to P-Det is rather small. In order to show these impacts for all EU-18 states, Table 8 provides $P\text{-}Det_{ADD}$ considering secondary and tertiary treatment, respectively. The data confirm which has been observed previously for some states, i.e. in general $P\text{-}Det_{ADD}$ is rather small (0.5-6.8%). As discussed above, this value depends on the type of STP technology and is more likely somewhere between the reported $P\text{-}Det_{ADD}$ values of secondary and tertiary treatment. For the EU-18 mean $P\text{-}Det_{ADD}$ will be between 2.4-4.2% (Table 8).

Table 8 : *Balancing ADD fraction in surface waters considering the current STP-situation according to EUROSTAT (2006). P-Det$_{ADD}$ = the P-fraction from ADD of the total P in surface waters*

Country	Connected to STP [% cap]	ADD P in surface waters (secondary STP treatment)		ADD P in surface waters (tertiary STP treatment)	
		1000 t/a	P-Det$_{ADD}$	1000 t/a	P-Det$_{ADD}$
Austria	86%	0.50	6.8%	0.15	3.7%
Belgium-Luxembourg	40%	0.60	6.5%	0.42	5.7%
Denmark	89%	0.37	6.0%	0.10	2.7%
Finland	81%	0.26	3.5%	0.09	1.7%
France	79%	2.86	4.2%	1.04	2.6%
Germany	93%	4.31	6.2%	1.01	3.0%
Greece	50%	0.35	2.8%	0.22	2.4%
Ireland	70%	0.11	2.4%	0.05	1.4%
Italy	75%	0.93	2.1%	0.37	1.4%
Netherlands	99%	0.77	5.9%	0.14	2.4%
Portugal	42%	0.08	0.6%	0.05	0.5%
Spain	89%	0.93	1.8%	0.25	0.9%
Sweden	93%	0.33	3.1%	0.08	1.1%
United Kingdom	88%	3.15	5.6%	0.89	3.6%
Czech Rep	72%	0.22	2.3%	0.09	1.6%
Hungary	57%	0.09	0.9%	0.05	0.7%
Poland	58%	0.21	0.6%	0.12	0.5%
EU-18	80%	16.1	4.2%	5.2	2.4%

The current analysis show, that the highest relative input of P into surface waters comes from human wastes and faeces and from agriculture through diffusive emissions. However, by looking at the relative fractions presented in this paper, it needs to be considered that P-concentrations in the local environment may vary considerably. These can significantly be driven by run-off of P from arable land, which is strongly dependent on specific environmental factors on soil characteristics and local fertilizer applications and/or by additional local point sources (e.g. industry or untreated sewage). Although the emissions of P from municipal wastewater is considered to be wide dispersive, the local source apportionment may be different compared to the generic picture on the country scale as given in this paper. Hence, while this paper solely focuses on the relative contributions of P from detergents in surface water, it cannot provide a conclusion on the aquatic risk potential of P (e.g. due to eutrophication). Recently, research to quantify eutrophication risk from detergent P on the regional scale in the context of the WFD has been published by the Spanish National Research Institute (INIA), who developed a probabilistic, higher tier risk assessment model for eutrophication [31]. Such higher tier risk assessments enable an evaluation of the effective contribution of detergent-P to the risk of eutrophication at regional levels.

5. CONCLUSIONS

Despite the fact that the source apportionment in this paper represents a generic picture of the overall situation in European countries, the data transparently show the relative significance of detergent P in the environment. P from municipal wastewater has been reduced significantly in countries with a high degree of connectivity to sewage treatment facilities. However, P- from detergents may account for up to approximately 30% in surface waters of countries, where sewage treatment is poor and P-containing laundry detergents are dominant. In countries where the market share of P-free laundry detergents is already 100% the remaining P from ADD has relatively little impact on the total P-Det. (1-6%). A similarly small impact was also calculated for the remaining EU-18. It seems evident that further significant reduction of P from municipal wastewater can be achieved by an improvement of the sewage treatment situation and/or by a replacement of P-containing laundry detergents. In fact, 'what-if' scenarios, that will be reported elsewhere [30], verify these assumptions. It can be concluded that ADD as P-source in the aquatic environment may not significantly contribute to the nutrient status, especially in eutrophication sensitive areas, where efficient P removal from sewages is regulated by the UWWTD.

REFERENCES:

[1] Behrendt H, Bach M, Kunkel R., Opitz D, Pagenkopf W-G., Scholz G., Wndland F. 2002. Quantifizierung der Nährstoffeinträge in die Öberflächengewässer Deutschlands auf der Grundlage eines harmonisierten Vorgehens. UFOPLAN-Nr.299 22 285

[2] Barr Engineering Company (2004) Detailed Assessment of Phosphorus Sources to Minnesota Watersheds. Report for Minnesota Pollution Control Agency. http://www.pca.state.mn.us/hot/legislature/reports/phosphorus-report.html

[3] European Environmental Agency - EEA (2005). Source apportionment of nitrogen and phosphorus inputs into the aquatic environment. EEA Report No 7/2005 Denmark ISSN 1725-9177

[4] Stiftung Warentest (2002) German Consumer association magazine - November 2002

[5] Suresh B. and Yonyama M. (2002) Industrial Phosphates. Chemical Economics Handbook Marketing Research Report. SRI Consulting International

[6] Lauriente D.H. (2003) Phosphate Rock. CHE Marketing Research Report. In Chemical Economics Handbook, SRI International

[7] Ifa Data Bank Fertilizer Consumption Statistics: N - P2O5 - K2O (2006)

[8] Glennie E. B., Littlejohn C., Gendebien A., Hayes A., Palfey R., Sivil D., Wright K.. (2002) Phosphates And Alternative Detergent Builders – Final Report. EU Environmental Directorate, WRc Ref.:UC 4011, WRC Swinton, England

[9] CEFIC (2004) Responsible Care Reporting 1996-2003. CEFIC Performance Data www.cefic.org

[10] Imhoff, K and Imhoff, K.R. (1993) Taschenbuch der Stadtentwässerung. 28th Edition. Oldenbourg Verlag, München Wien

[11] Metzner G. 2001. Phosphates in Municipal Waste water – An analysis of input and output in sewage treatment. Tenside Surf. Det. 38, 6. 360-367

[12] Folke, J., (1996) "Phosphate, Zeolite and Citrate in Detergents—Technical and Environmental Aspects of Detergent Builder Systems". Report No. 95002/06, written by MFG—Environmental Research Group, Gilleleje, Denmark, for Kemisk Tekniska Leverantörförbundet, Stockholm.

[13] CEFIC (2003) Detergent phosphates: a sustainable detergent component – background information. www.ceep-phosphates.org

[14] Henkel (2005) internal marketing survey

[15] IKW-Umfrage (2004) Erhebung der Einsatzmengen bestimmter Inhaltsstoffe von Haus Wasch-, -Putz/Pflege- und Reinigungsmitteln zum Einsatz in Deutschland 1994-2004

[16] IBM (2002): AISE Code of Environmental Practice: Final Report for the European Commission 1996-2001, report prepared for AISE.

[17] Floyd P., P. Zarogiannis and K. Fox (2006) Non-Surfactant Organic Ingredients And Zeolite-Based Detergents. Final Report, June 2006; Risk & Policy analysis Limited (RPA), UK

[18] Smulders E. (2002) Laundry Detergents. Wiley-VCH Verlag GmbH, ISBN 3-527-30520-3

[19] Eastham R.D. (1981) Interpretation klinisch-chemischer Laborresultate, 2nd Edition, Verlag S. Karger, Basel, München.

[20] EUROSTAT (2006) Bevölkerungsanteil mit Anschluss an kommunale Kläranlagen insgesamt (in %) http://epp.eurostat.ec.europa.eu (statistical Data)

[21] ATV-DVWK (2003) Phosphorrückgewinnung. KA-Abwasser, Abfall 2003 (50) 6

[22] FAOSTAT (2006) Homepage: www.fao.org (statistical Data)

[23] Schreiber, H., Behrendt, H., Constantinescu, L., Cvitanic, I., Drumea, D., Jabucar, D., Juran, S., Pataki, B., Snishko, S. & Zessner, M. (2003): Harmonised Inventory of Point and Diffuse Emissions of Nitrogen and Phosphorus for a Transboundary River Basin, Final Report, Institute of Freshwater Ecology and Inland Fisheries, Berlin, 158 pp.

[24] Sibbersen E., Runge-Metzger A. (1995) Phosphorus Balance In European Agriculture - Status And Policy Options. In: SCOPE 54 Phosphorus in the Global Environment - Transfers, Cycles and Management, H. Tiessen ed., 1995, 480 pp

[25] EUROHARP Quantification Tools. 2006. Toolbox for European Harmonised Procedures for Quantification of Nutrient Losses from Diffuse Sources http://www.euroharp.org/toolbox/qt1.php

[26] OSPAR (2003). Nutrients in the Convention area Inputs of Nutrients into the Convention area Implementation of PARCOM Recommendations 88/2 and 89/4 Eutrophication and Nutrients Series OSPAR Commission, 2003. ISBN 1-904426-16-6

[27] UBA (2001) Umweltpolitik Wasserwirtschaft in Deutschland Teil III – Emissionen in die Oberflächengewässer und Meere; http://www.umweltbundesamt.de

[28] HELCOM (2004) The Fourth Baltic Sea Pollution Load Compilation (PLC-4) Balt. Sea Environ. Proc. No. 93

[29] European Environmental Agency - EEA (2002) Indicator Fact Sheet (WEU02): Nitrogen and Phosphor in rivers. http://themes.eea.eu.int/Specific_media/water/indicators

[30] Wind T. 2007. Detergent Phosphates and Their Environmental Relevance in Future European Perspectives, Tenside, Surfactants, Detergents, 44 (1), 19-24

[31] De Madariaga, B.M., Ramos, M.J., and Tarazona, J.V. Model implementation and quantification of the eutrophication risk associated to the use of phosphates in detergents. Final study report. Green Planet Research Report GPR-CEEP-06-2-Final. 2006. Carried out by Green Planet Research and INIA (Spanish National Institute for Agricultural and Food Research and Technology) for CEEP. Published by the EU Commission at: http://ec.europa.eu/enterprise/chemicals/legislation/detergents/index_en.htm