% Molybdate Reactive Phosphorus of Total Phosphorus in Urban Wastewater Influents and Effluents in County Cork Agglomerations >2000 P.E

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by

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Abstract

Phosphorus is a key nutrient in freshwater ecosystems as it is well known to cause severe water quality problems when enrichment with phosphorus occurs, a phenomenon known as eutrophication. Legislative measures are in place to control or limit the amount of phosphorus discharged, and there are several physical, chemical and biological treatment processes used to remove or reduce phosphorus prior to discharge. Whether or not rural developments are granted planning permission in Ireland is often contingent on the levels of phosphorus in the receiving waters it is proposed to discharge treated effluent to.

Several forms of phosphorus exist in environmental monitoring; the most often encountered is the inorganic form usually known as orthophosphate. However, there are other names used for this inorganic form, depending on the method of analysis, such as soluble reactive phosphorus (SRP), molybdate reactive phosphorus (MRP), dissolved reactive phosphorus (DRP), leading to confusion and misinterpretation of results. The presentation of analytical data also leads to confusion when the results' form is not clearly expressed.

Average wastewater influent total phosphorus levels for County Cork's wastewater treatment plants vary considerably. Average phosphorus loadings were in the range 2.3 to 14.2 mg/l TP-P, although a more reliable upper end of the range for average influent TP-P in Cork is Ballincollig with 11.6 mg/l TP-P. Average influent MRP ranged from 1.6 mg/l to 7.6mg/l PO_4-P. Average MRP% of the total phosphorus ranged from 43.5% to 68 %.

Disregarding effluents where phosphorus removal measures are required under the Urban Waste Water Treatment Regulations, 2001, average effluent concentrations of total phosphorus ranged from 1.1mg/l at Kanturk to 6.4mg/l TP-P at Ballincollig. Average effluent concentrations of MRP ranged from 0.9 to 4.6mg/l PO_4-P. The range of % MRP of the total phosphorus was greater in plants where phosphorus removal technologies were employed, 34.4% to 91.7%. Plants without additional phosphorus removal had a narrower range, 62.4% to 87.1%.

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My employer, Cork County Council, particularly Louis Duffy as Director of Service, Environment, whose approval allowed me the opportunity to complete the M.Sc.

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1 Introduction to Project

1.1 Project Objectives

Currently, under Irish Legislation, the discharge of any waste water to waters, as defined, requires the discharge to be in accordance with a discharge license issued under Section 4 of the Local Government (Water Pollution) Acts, 1977 to 2007.

Previously exempted discharges included <5m^3/day domestic wastewater to percolation, and a discharge from a sanitary authority arising from their function. The Water Services Act (2007) and the Wastewater Discharge (Authorization) Regulations (2007) respectively remove these exemptions.

The application for such a license under Section 4 requires an assimilative capacity and a mass balance to be undertaken in accordance with the Local Government (Water Pollution) Act, (1977) Water Quality Standards for Phosphorus Regulations, (1998) to establish whether the receiving waters can assimilate the new discharge without an adverse effect.

Parameters usually required for an assimilative capacity study include biochemical oxygen demand, suspended solids, nitrates and ammonia but most significantly and often contentiously, phosphate (or to give it its proper name as required under the Phosphate Regulations, "molybdate reactive phosphorus").

Whilst working in the assessment and licensing of these wastewater discharges to waters, one frequently encounters various types of phosphates, with the names switching forms and meaning. Applicants often are unsure which type they are actually referring to, which they should be referring to, whether they are referring to phosphate as P or just phosphate, the significance of which cannot be stressed enough, as a phosphate concentration expressed as PO_4 will appear 3 times higher than if it was expresses as PO_4-P (refer to section 7.2).

Published literature on the subject suffers the same lack of consistency (Thabano et al 2004; Nkegbe et al 2005). House, an eminent authority on environmental phosphorus and its effects, in 1995, calls MRP 'Murphy and Riley Reactive Phosphorus' (House, 1995), but in 2002 calls it 'Molybdate Reactive Phosphorus' (House, 2002). According to Haygarth (2000) there is an urgent need for a systematic and logical method of classification. Purists differ on which form exactly is which, and the correct terminology to use when discussing the forms of phosphorus. Purists assume that orthophosphate has been filtered, while molybdate reactive phosphorus has not, unless stated. Please refer to section 7.2.2 for a more detailed discussion of the various forms of phosphate, and how confusion could arise.

Total phosphorus is the type of phosphorus measured and reported when discussing wastewater discharges. However assimilative capacity studies under the phosphorus regulations require the study to be on the molybdate reactive phosphorus. General assumptions are made on % composition of total phosphorus, with an often encountered figure of 80% orthophosphate of the total phosphate, and it is used as a rule of thumb in such calculations. In 5 years of license application assessments I have been unable to locate a reference for this figure, although experience in the analysis of wastewaters suggests the % varies greatly depending on treatment process and quality of effluent. Very little information exists on the % orthophosphate composition of the total phosphorus in an influent, particularly with regard to Irish urban wastewaters.

1.2 Project Aims

The aim of this dissertation is to compile is currently known about phosphorus from a general wastewater perspective. Whilst not getting into too much detail in any one area, the dissertation should provide the reader, particularly undergraduates or a lay person with a good grounding, insight and understanding of phosphorus and wastewater, relevant Irish legislation, and whetting their appetite should they decide to probe the subject further.

Starting with a brief introduction to the geology, extraction and uses of phosphorus, the dissertation progresses into how phosphorus gets into wastewaters and the environment from different inputs, and the types of phosphorus encountered in wastewater treatment and analysis. The effect of excess phosphorus on an aquatic system, and the legislative measures to control discharges of phosphorus, and a brief summary of wastewater treatment techniques currently used to control phosphorus in discharges are found in this chapter.

The various forms of phosphorus and phosphate encountered in environmental monitoring are clearly explained, when each form is used, and why confusion is arising over which one should be used.

Finally an analysis of the influent/ effluent streams of several wastewater treatment plants in Cork is given, and the % orthophosphate of the total phosphate is presented, along with % removal where possible to investigate whether there is any substance to the 80% rule of thumb.

Suggestions for future research are presented and rationale why this work would be useful.

Summary of project objectives:

- Give a broad introduction to phosphorus, its uses, and its environmental impact
- Introduce and explain the various forms of phosphorus compounds, particularly orthophosphate, and how confusion is arising as to their use/misuse
- Investigate whether there is any substance to the 80% rule of thumb.

1.3 Dissertation Structure

The dissertation can be considered as being in two parts, with Chapters 2 to 6 inclusive a literature review of phosphorus from an environmental impact perspective. Chapter 1 introduces the topic, study area, rationale and aims of the project. Chapters 2 to 6 inclusive are general topics of relevance to phosphorus. Chapters 7 and 8 are more analytical and technical, and the actual analytical results of the investigation are presented in Chapter 9. Chapter 10 discusses the findings of the project and suggests areas for future research.

Chapter 2 introduces phosphorus, its geology and mineralogy, explains the extraction and manufacture of the phosphorus compounds used in industrial and manufacturing processes with particular attention to its use in detergents, which are of great significance in domestic wastewaters. Its biological function is also briefly discussed.
In Chapter 3 and 4 the phosphorus cycle is explained, and the impact of the various inputs of phosphorus into the environment are explained, with particular attention to anthropogenic eutrophication of aquatic systems, and the cause and effects of increased phosphorus levels in an aquatic system.

European and National Legislative measures to control phosphorus inputs are outlined in Chapter 5, including how these measures are being implemented in Ireland and other European countries. Particular attention is given to the European Union's Water Framework Directive (2000), The Phosphorus Regulations (1998) and the Urban Wastewater Directive (1991). Irish planning policy with regard to phosphorus and some examples of contentious planning application cases where phosphorus was the significant factor in the Authority's decision are given.

Chapter 6 discusses wastewater treatments with particular attention to the various physical, chemical and biological removal/reduction mechanisms of phosphorus in the discharge are explained. The types of phosphorus encountered in wastewater are also explained.

Chapter 7 discusses the forms of phosphorus encountered in environmental phosphorus monitoring, the analytical techniques used to identify the various forms, and how confusion can arise over the myriad forms of phosphorus discussed in the literature and trade.

Chapter 8 explains the method and materials used in the analytical part of the project. Chapter 9 presents the results of the investigation on a treatment plant by treatment plant case, the phosphorus removal mechanisms (if any) in each plant, and the percentage orthophosphate of the total phosphorus in the influent and treated final effluent, and Chapter 10 discusses the findings of the analytical investigation, the effectiveness and future for legislative phosphorus controls, and suggests areas for further study.

1.4 Study Area: County Cork

All statistics in section 1.4, unless specified, are taken from Cork County Council County Development Plan, 2007.

1.4.1 Location

With an area of 7,454 km², and a coastline over 1000km Cork is the largest county in Ireland, and comprises 1/8 of the Republic. The county is bordered to the west by County Kerry, to the north by County Limerick, the northeast by South Tipperary and the east by County Waterford, and to the south and south west by the Atlantic and the south by the Celtic Sea. The second largest city in the state, Cork City, is the largest centre for population, employment, commerce and services after Dublin.

The centre of the county is dominated by three rivers and their valleys, the Bandon, the Blackwater and the Lee, all flowing from west to east across the county. These areas are noted for their rich biological diversity, providing habitats for rare fish and invertebrates such as salmonids, lampreys, freshwater pearl mussel and crayfish.

To the west lie the Derrynasaggart and Boggeragh Mountains and to the northeast the Galtee Mountains. The rugged coastline and islands of the southern and south-western part of the County support reefs, sea cliffs, rocky inlets and bays.

A number of sites in County Cork have been identified to be of exceptional importance as habitats for wildlife and to this end have been or will be designated for protection under European and/or national legislation as Natural Heritage Areas (NHAs), Special Protection Areas (SPAs) or Special Areas of Conservation (SACs). With 8 NHAs and a further 126 proposed, 29 candidate SACs, 13 SPAs, Cork County has a rich ecological heritage.

1.4.2 Population

The 2006 Census records that the population of the County (including Cork City) was 481,295 persons, an increase of 7.5% from the 2002 census. An increase of 127,059 people is projected for the year 2020. Until 1996, population trends were largely determined by labour market conditions in Ireland with a long-term trend towards significant levels of emigration with the domestic population remaining broadly static. Since 1996, population trends in Ireland and Cork County have changed dramatically. Fuelled by strong domestic growth, the national GDP has grown by an average of 10.1% per annum over the last 5 years (the highest growth rate in the EU) there was a strong net immigration trend until towards the end of 2008.

The 1996 County Development Plan forecast that the County's population would rise to 311,900 by 2001. The 2002 Census found that the population had reached 324,767. The 2003 County Development Plan estimated that the County's population would reach 365,300 by 2011. The 2006 census found the population had already reached 361,877. This rapid population growth in recent years has led to serious pressures on the existing infrastructure in the County. Infrastructure such as water services, social and transport, planned on the basis of earlier population forecasts has often not had sufficient capacity to match the demand arising from the levels of population growth that have been achieved.

Table 1: Population and Households – County Cork 1996 - 2006

	1991	1996	2002	2006	2020 (Projected)
Population	**283,100**	**293,323**	**324,767**	**361,877**	**458,354**
Households	**80,200**	**88,933**	**105,248**	**123,295**	**185,751**
Average Household Size	**3.53**	**3.30**	**3.09**	**2.94**	**2.46**

1.4.3 Wastewater Disposal in County Cork

The major centres of population (>2000PE) require the implementation of the national "Urban Wastewater Regulations", in order to comply with EU requirements. Upgrading of networks in existing wastewater schemes, and new treatment facilities will be required to comply with this directive.

Major new treatment plants are required in Bantry, Castletownbere, Schull, Skibbereen, Carrigaline, Cobh, Kinsale, Passage West/Monkstown, Ringaskiddy, Whitegate/Aghada and Youghal. Major upgrades of existing treatment plants are required in Mitchelstown, Millstreet, Newmarket, Clonakilty, Dunmanway, Ballincollig, Blarney/Tower, Carrigtwohill, Macroom and Midleton. The proposed Lower Harbour Wastewater Scheme will be one of the largest in the County when complete and treat effluent from most of the towns in the harbour area including Passage West / Monkstown, Cobh, Carrigaline, Crosshaven and Ringaskiddy (Cork County Council County Development Plan, 2007).

Capital expenditure is largely funded through the Department of the Environment, Heritage and Local Government, whilst planning and management of services are carried out at local authority level. The engineering of major new works is normally contracted out by the local authority. At a local level, provision for funding is made through the Water Services Investment Programme.

From 2000 to 2006, almost €3 billion has been invested nationally upgrading 210 wastewater treatment plants. The 2007-20012 Water Services investment programme comprises 955 projects with a capital budget of almost €6 billion, with €485,489,000 allocated to Cork County Council (DoEHLG September, 2007).

The most recent assessment is expressed in the Cork County Council Water Services Assessment of Needs 2006 will require over €2.5 billion capital investment, the more significant schemes for 2007-2012 include:

- Mitchelstown Sewerage Scheme (Nutrient Removal) € 221,000
- Ballyvourney/ Ballymakeery Sewerage Scheme € 3,049,000
- Kinsale Sewerage Scheme € 20,000,000
- Midleton Sewerage Scheme (Infiltration Reduction) € 2,078,000
- North Cork Grouped DBO Wastewater Treatment Plant € 5,150,000
- Skibbereen Sewerage Scheme € 20,000,000
- Mallow Sewerage Scheme € 5,408,000
- Bandon Sewerage Scheme € 14,729,000
- Garrettstown Sewerage Scheme € 2,153,000
- Little Island Sewerage Scheme € 2,200,000
- Bantry Sewerage Scheme € 7,148,000
- Dunmanway Sewerage Scheme € 2,153,000
- Millstreet Wastewater Treatment Plant (Upgrade) € 1,628,000
- Ballincollig Sewerage Scheme (Upgrade) € 22,248,000
- Cork Lower Harbour Sewerage Scheme € 73,542,000
- Shannagarry/ Garryvoe/ Ballycotton Sewerage Scheme € 3,780,000
- Youghal Sewerage Scheme € 14,420,000
- Clonakilty Sewerage Scheme (Plant Capacity Increase) € 3,677,000
- Courtmacsherry/ Timoleague Sewerage Scheme € 2,472,000
- North Cobh Sewerage Scheme € 3,193,000
- Ballylicky Sewerage Scheme € 2,153,000
- Baltimore Sewerage Scheme € 3,162,000
- Castletownbere Sewerage Scheme € 5,202,000
- Schull Sewerage Scheme € 3,523,000
- Mitchelstown Sewerage Scheme € 3,000,000
- Newmarket Sewerage Scheme € 3,152,000

- Carrigtwohill Sewerage Scheme € 20,000,000
- Macroom Sewerage Scheme € 5,150,000
- Glengarriff Sewerage Scheme € 2,500,000
- Roscarberry/Owenahincha Sewerage Scheme € 1,576,000

1.4.4 Wastewater disposal in County Cork

There are currently 23 agglomerations greater than 2000 PE under the control of Cork County Council. Of these, 16 are currently served by a wastewater treatment plant providing greater than primary treatment. The locations of the 14 plants used in this study are identified on fig. 1 below. For operational reasons, Macroom and Carrigtohill were omitted. During the course of the project, construction commenced on several agglomerations not served by a treatment plant.

Figure 1 Co. Cork showing location of wastewater treatment plants used in study

2 Introduction to Phosphorus

Chapter Overview

Chapter 2 introduces phosphorus, its chemical properties, geology and mineralogy, explains the extraction and manufacture of the phosphorus compounds, their use in products with particular attention to its use in detergents, which are of great significance in domestic wastewaters. Its biological function is also briefly discussed.

2.1 Phosphorus

Phosphorus (from the Greek: phôs meaning "light", and phoros meaning "bearer"), is an important element for all forms of life. Due to its high reactivity, phosphorus is never found as a free element in nature. Its chemical symbol is P. Phosphorus, an element in Group 5, has the atomic number 15 and its atomic weight is 30.97g. In its pure form it is a waxy white non metallic solid and spontaneously catches fire in air, burning to P_4O_{10}. Discovered in 1669, by Henning Brand, a German alchemist who by heating urine (50 buckets of soldiers urine (Bryson, 2003)) without air, isolated a white substance, which after a while began to glow, and when exposed to air, combusted.

Phosphorus is the eleventh most abundant element in the lithosphere. Owing to its reactivity, it is generally associated with calcium (Ca), sodium (Na), fluorine (F), chloride (Cl), metals such as iron (Fe), aluminum (Al), magnesium (Mg), heavy metals, for example cadmium (Cd), and radionuclides like uranium (U) etc.

2.2 Phosphorus Rocks and Minerals

Although present in the main sedimentary and igneous rocks, 80% of mined phosphorus today is derived from sedimentary rocks. Most igneous rocks contain small amounts of phosphorus. The phosphate content in rocks currently mined, ranges from 5 to 40% P_2O_5, which after processing increases the content to between 32% to 42% P_2O_5 (Glennie et al 2002). Extraction and production values for phosphorus are reported as P_2O_5, phosphorus pentoxide. Highest percentages found in sedimentary rocks are in the Taiba mine in Senegal at 37.5%, whilst the highest in igneous rocks are found in the Phalaborwa mine in South Africa (RIZA, 2002).

Common phosphorus containing minerals found in rocks include:

Apatite ($Ca_5(PO_4)_3(OH, F, Cl)$) from the Greek apatao –
"I am misleading". Apatite is a group name of three related minerals, depending on amount of fluoride (Fluorapatite), chloride (Chlorapatite) or the hydroxyl group (Hydroxylapatite).

Vivianite ($Fe_3^{+2}(PO_4)_2.8(H_2O)$), after the English mineralogist, J. G. Vivian, is a sedimentary mineral associated with organic deposits.

Wavellite ($Al_3(PO_4)_2(OH)_3F_{0.5}.5(H_2O)$) after William Wavell (1829) who discovered the mineral, is common in metamorphic rocks.

Brushite $Ca(HPO_4).2(H_2O)$ is the mineral found in guano deposits.

2.3 Phosphorus Extraction and Beneficiation

Large scale surface methods are mostly used (UNEP, 2001). Most phosphate extraction uses opencast dragline or open pit excavator methods. India, Morocco, Mexico and Tunisia with their deeper ore bodies employ underground methods.

Beneficiation processes increase the phosphorus content, and remove impurities and contaminants. The phosphorus content of the mineral determines the amount of beneficiation required, although some phosphorus ores are of sufficient quality to be applied to land following screening and crushing (UNEP, 2001).

Heavy metal contaminants such as uranium, cadmium, nickel, chromium, copper and zinc, are present at higher concentrations in sedimentary rocks than in igneous. The presence of radioactive elements can be a significant aid in exploration for deposits. Of particular concern is cadmium, leading to limits being set for the cadmium content in the fertilizer used in some European countries (Glennie et al 2002).

Of 131 million tons of phosphate rock mined to give 40.8 million tons mineral phosphorus pentoxide (P_2O_5), 80% was used in mineral fertilizers, chiefly diammonium phosphate and monoammonium phosphate, 12% used in detergents, 5% in animal feeds and the remaining 3% used in food, pharmaceutical and metal sectors (Nilson,1995).
(With the atomic weight of phosphorus 31 atomic mass units (amu), and oxygen 16 amu, the total molecular weight of P_2O_5 is 142 amu. Therefore the % phosphorus in P_2O_5 is 44%. To convert P_2O_5 to P, divide by 2.3, to convert P to P_2O_5 multiply by 2.3).

The major producers such as United States (12.8 million tons P_2O_5 - 75% of which comes from Florida) followed by Morocco (6.4 million tons P_2O_5) dwarf the total European output of 0.36 million tons. Morocco's reserves of phosphate ores are approximately 6 times that of the United States, giving Morocco the potential to be the leading exporter of phosphorus (IPR, 2008). In 2007, Morocco produced around 50% of all exported phosphate rock, and is the main controller of rock prices (the US does not export phosphate rock). Average price/ton of phosphate rock grew form \$32.50 in 2006 to \$51.36 in 2008 (USGC, 2008).

The main methods used for phosphate extraction and purification are the ‘thermal route’ and the ’wet route’. The thermal process produces purest initial product, but is energy intensive, and vulnerable to contaminants such as iron impacting on the process. 93% of US phosphate was manufactured using the wet process. One plant in America, the Monsanto Plant at Soda Springs, Indiana, is the only thermal phosphorus plant in the US (the elemental phosphorus is used to manufacture phosphorus trichloride, a chemical intermediary for the manufacture of glyphosate-base herbicides). Globally, thermal route accounts for 65% of the phosphoric acid produced (USGS, 2008).

2.3.1 Thermal Route

In the thermal route the phosphate ore is mixed with clay in a ball mill to form 10mm diameter pellets, which are then baked in a carbon monoxide atmosphere to remove fluorine. The dried pellets are baked, mixed with coke and gravel and added to an electric furnace at 1200°C to 1500°C.

$$2Ca_3(PO_4)_2 + 6SiO_2 + 10C \rightarrow 6CaSiO_3 + P_4 + 10CO \qquad \text{Eqn. 1}$$

The Phosphorus, leaves the furnace in the gas phase, and is condensed and stored under water. This whole operation is carried out in an oxygen-free atmosphere (Duley, year unknown). The molten calcium silicate is tapped off and allowed cool. This calcium silicate is slightly radioactive, as uranium is often associated with phosphorus deposits (Glennie et al 2002). Volatile metals including cadmium are extracted in the gaseous phase and captured in cyclones or scrubbers.

If iron is present in the ore, it can cause significant problems, causing loss of energy and reduced product. Iron concentrations of <1% are preferred. Iron reacts to form ferrophosphorus (FeP):

$Fe_2O_3 + 3C + 2P \rightarrow 2FeP + 3CO$ Eqn.2

The phosphorus is burnt in air, and the product (P_2O_5) contacted with very dilute phosphoric acid to produce more phosphoric acid.

$P_4 + 5O_2 \rightarrow 2P_2O_5$ Eqn.3

$P_2O_5 + 3H_2O \rightarrow 2H_3PO_4$ Eqn.4

The phosphoric acid produced is very pure, with only arsenic present as a contaminant. Dearsenification is required by either the hydrogen sulphide or sodium sulphide route, before it is available for higher grade processes such as food and pharmaceutical applications, and electronic industry (RIZA)[1].

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[1] Rijksinstituut voor Integraal Zoetwaterbeheer en Afvalwaterbehandeling – (Dutch) Institute for Inland Water Management and Waste Water Treatment).

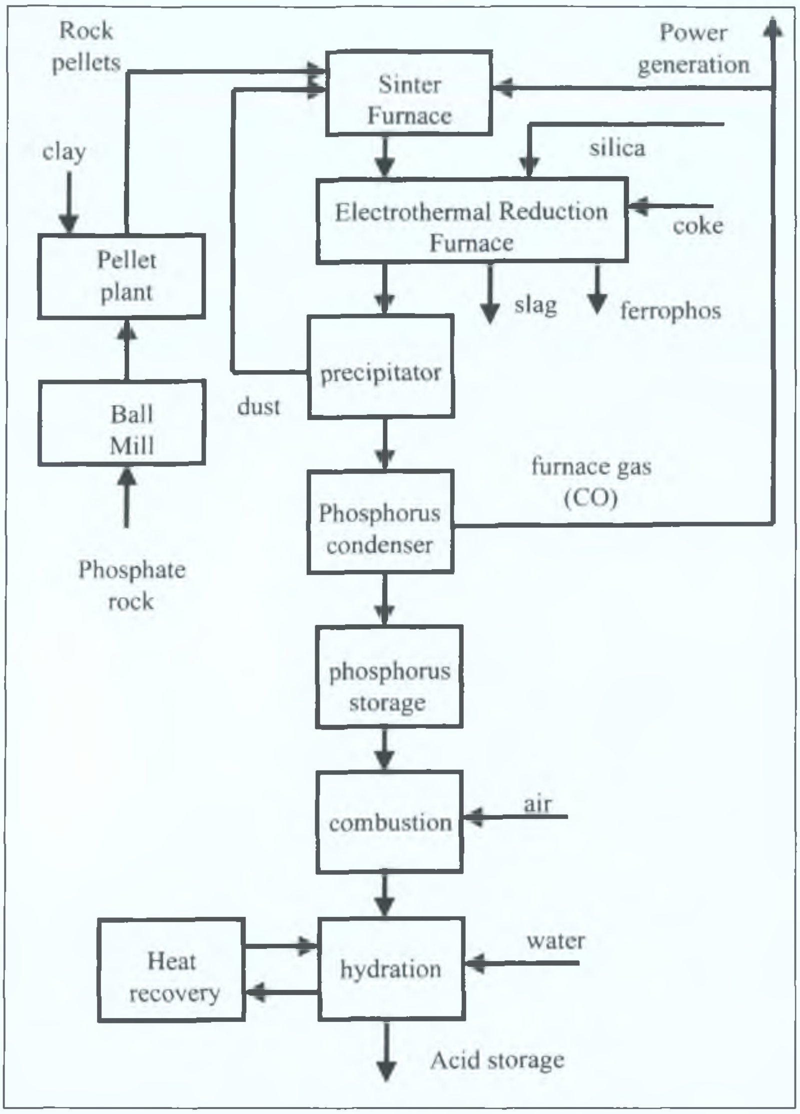


Figure 2. Thermal Route (Driver, 1999)

2.3.2 Wet Route

In the wet route sulphuric acid, or less commonly hydrochloric acid, is mixed with finely ground phosphate rock to produce phosphoric acid.

$$Ca_3(PO_4)_2 + 3H_2SO_4 \rightarrow 3CaSO_4 + 2H_3PO_4 + 3H_2O \qquad \text{Eqn. 5}$$

The process produces phosphoric acid of 26-32% P_2O_5. The phosphoric acid may be used directly in fertilizers, or further purified in a cross stream solvent extraction system followed by dearsenification using Na_2S to produce high purity phosphoric acid.

Calcium sulphate, also known as phosphogypsum ($CaSO_4$. $2H_2O$) is a waste byproduct and contains the impurities. As it is slightly radioactive, its use is restricted. For every ton of phosphoric acid produced, five tons of phosphogypsum are produced and stockpiled (Florida Institute of Phosphorus Research, 2008). It is widely used in Japan as a substitute for “rock gypsum”.

Wet route can be subdivided into five process, with varying P_2O_5 efficiencies, quality of gypsum produced and energy consumed (RIZA, 2000);

1. Dihydrate process (operated by most plants)
2. Hemihydrate process

And three recrystallization process;

3. Hemihydrate recrystallization process
4. Hemi-dihydrate process
5. Di-hemihydrate process.

The wet route has the advantage of being less energy intensive but the phosphoric acid initially produced, called green acid) is of greater impurity. It is only recently that improvement in subsequent stages of processing allowed phosphoric acid produced by the wet route to be used in pharmaceutical and food sectors (Duley).

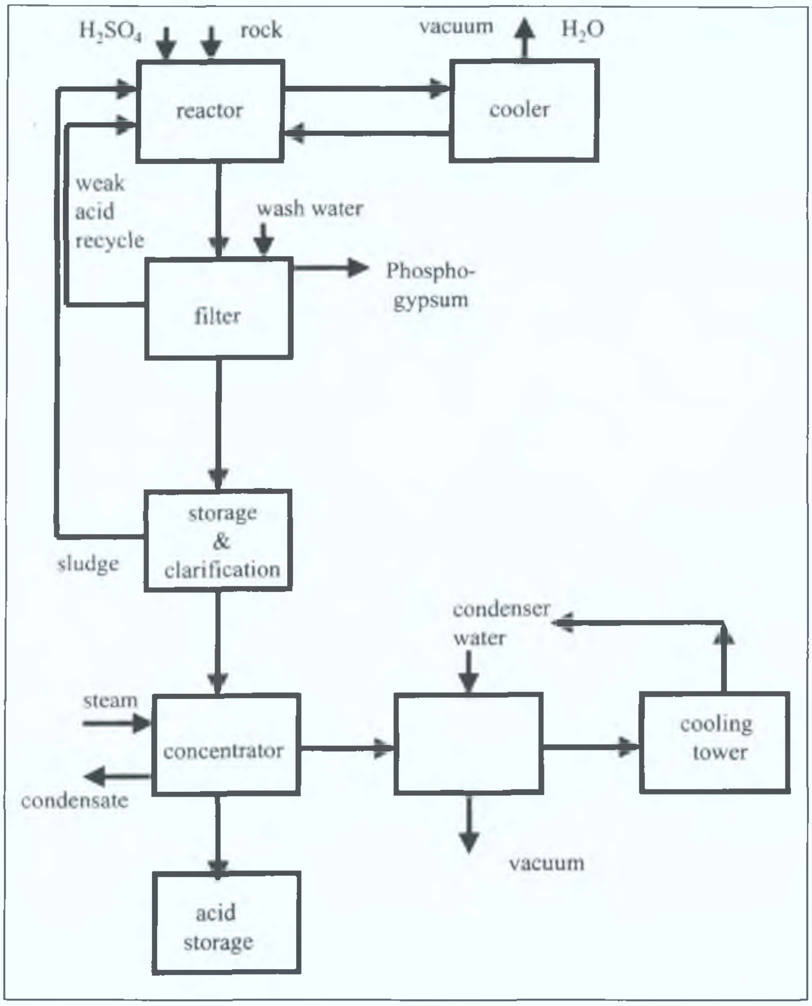


Figure 3. Wet Route (Driver,1999)

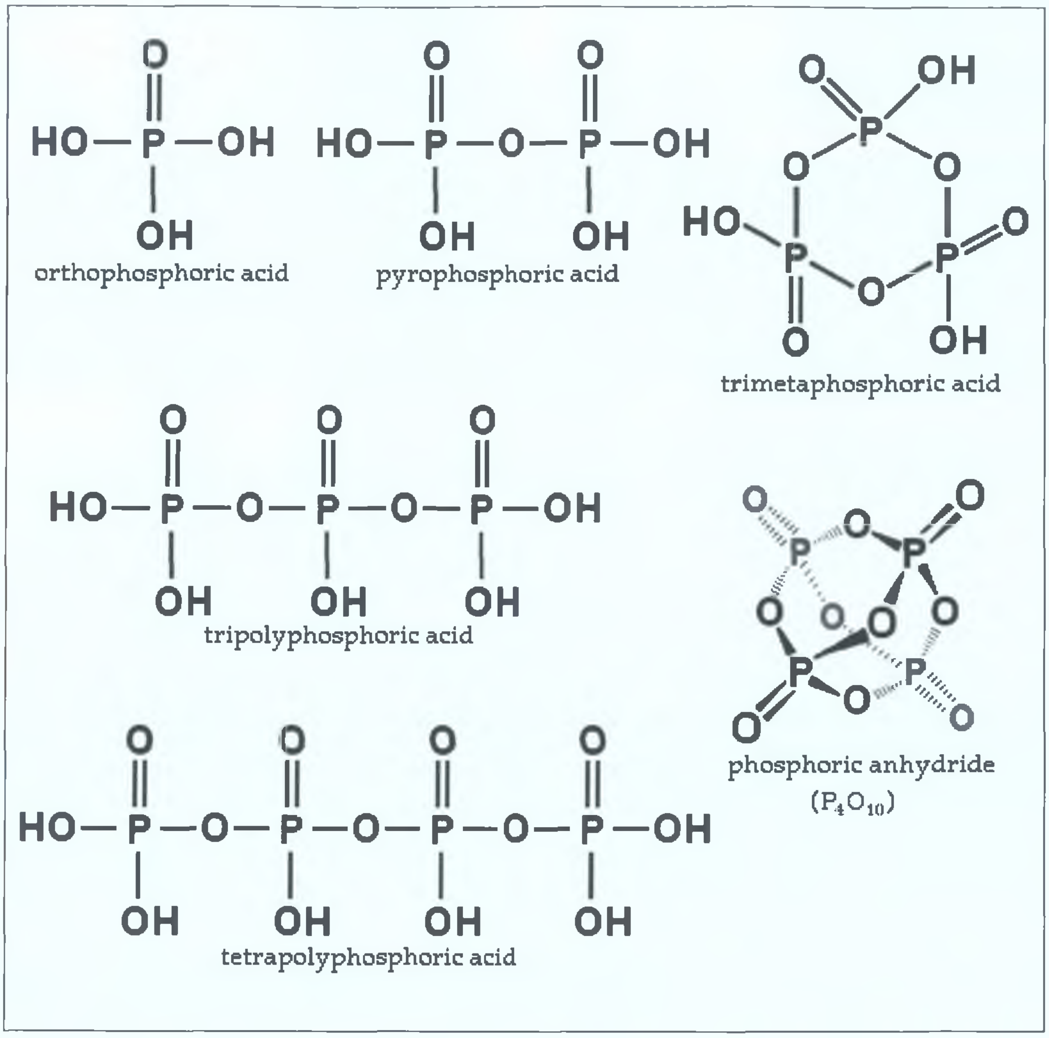


Figure 4. Common phosphoric acids (Padleckas, 2006)

2.4 Biochemical Phosphorus

As phosphate (PO_4), phosphorus makes up an important part of the structural framework that holds Deoxy Ribose Nucleic Acid (DNA). DNA contains the genetic instructions used in the development and functioning of all known living organisms.

Chemically, DNA is a long polymer of simple units called nucleotides, with a backbone made of 2-deoxyribose sugars and phosphate groups joined by ester bonds. Attached to each sugar is one of four types of molecules called bases; Adenine, Thymine, Guanine, Cytosine.

Phosphate is also an important structure in Ribonucleic acid (RNA) , although structurally similar to DNA, RNA is usually a single helix, has the base Uracil rather than Thymine, and has ribose sugars. RNA is involved in protein synthesis and decoding the genetic code.

Living cells also use phosphate to transport chemical cellular energy via adenosine triphosphate (ATP). Nearly every cellular process that uses energy obtains it in the form of ATP. Phosphorylation is the addition of a phosphate (PO_4) group to a protein molecule or a small molecule changing its structure and function but also storing chemical energy within the molecule for later use. Phospholipids are the main structural components of all cellular membranes. Calcium phosphate salts assist in stiffening bones.

Like calcium, phosphorus is important to vertebrates. An average adult human contains 11-12 g/kg body weight is phosphorus, about 85% of which is present in bones and teeth in the form of apatite, and the remainder inside cells in soft tissues. The human nutritional need for phosphorus is about 1.6g P/person/ day (Nilsson, 1995).

2.5 Phosphorus Applications

Concentrated phosphoric acids, which can consist of 70% to 75% P_2O_5 are very important to agriculture and farm production in the form of fertilizers. Global demand for fertilizers led to large increases in phosphoric acid production in the second half of the 20th century.

Other uses of phosphates include (CEEP, 1997):

- Phosphoric acid is used in food applications such as soda beverages.
- Sodium Monofluorophosphate is used in toothpaste.
- Trisodium phosphate is used in cleaning agents to soften water and for preventing pipe/boiler corrosion.
- Organophosphorus compounds, manufactured via the intermediate phosphorus chloride and the two phosphorus sulfides: phosphorus pentasulfide (P_4S_{10}), and phosphorus sesquisulfide (P_4S_3) have many applications, including in plasticizers, flame retardants, insecticides such as paraoxon, parathion and Malthion and industrial poisons such as tri-o-creysl phosphate (TOCP).
- Phosphorus is also an important component in steel production, in the making of phosphor bronze, and in many other related products.
- White phosphorus is used in military applications (known as Willy Pete) in incendiary bombs, smoke bombs and in tracer ammunition. Exposure to white phosphorus can result in 'phossy jaw', a condition in which the jaw bone disintegrates. http://www.globalsecurity.org/military/systems/munitions/wp.htm
- Red phosphorus is combined with iodine to form hydriodic acid (HI) which is then used to convert ephedrine to methamphetamine. (Matches are used as the source of red phosphorus to make illegal street methamphetamines). http://www.usdoj.gov/dea/index.htm
- In trace amounts, phosphorus is used as a dopant (an impurity deliberately added to a semiconductor) for N-type semiconductors to improve electrical conductivity
- ^{32}P and ^{33}P are used as radioactive tracers in biochemical laboratories.
- Sodium tripolyphosphate is used in detergents and the food industry.

2.6 Sodium Tripolyphosphate & Detergents

Sodium tripolyphosphate, or STPP ($Na_5P_3O_{10}$) is the main phosphate builder used in detergents. Builders, along with surfactants, stain removers, anti-redeposition agents, perfumes, are an important component of detergents. STPP can contribute 25 to 50% of the soluble phosphorus in domestic wastewater if STPP detergents are used (Glennie et al 2002)

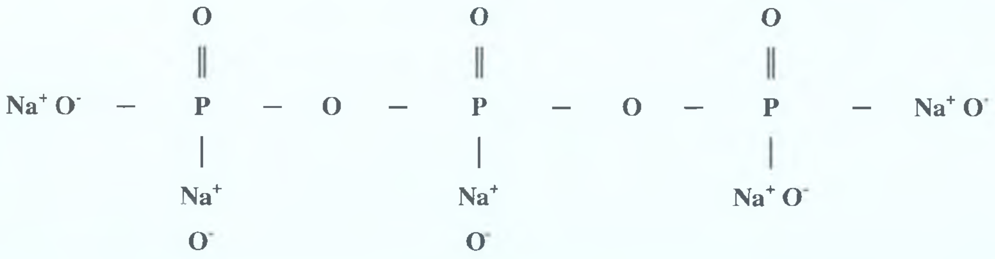


Figure 5 Sodium tripolyphosphate (**www.hellochem.com**) 2009

2.6.1 How detergents work:

Builders are required to reduce water hardness which decreases surfactant efficiencies, create alkalinity for optimal soil removal, assist in solubilization of other detergent components, allow dispersion of dirt and prevent its redeposition and facilitate manufacturing and consumer handling of the powder granules. 70% of the builders produced are used in laundry detergents, 15% in dishwasher detergents, and 15% in industrial detergents (Glennie, 2002)

Prepared by the neutralization of phosphoric acid with sodium ash to give sodium hydrogen phosphate. Sodium dihydrogen phosphate is added to the sodium hydrogen phosphate and heated at 500°C to produce the stable STPP.

$$2Na_2HPO_4 + NaH_2PO_4 \rightarrow Na_5P_3O_{10} + 2H_2O \qquad \text{Eqn.6}$$

STPP can be produced to food grade purity for use in the food sector, and is an authorised food ingredient under EU legislation (Directive 95/2), registered as E451. Uses of polyphosphates in the food sector include improving shelf life of food stuffs, and increasing the water binding capacity of proteins (CEEP).

STPP is the major non fertilizer phosphorus product, and is regarded by the chemical and food industry as the main bulk phosphorus ingredient in food and chemical sectors (Glennie 2002). According to Halliwell et al (2000) detergents may contain as much as 40% triphosphate in the formulation.

The European STPP industry contributes less than 10% to global STPP production. Major manufacturers are China and India. Phosphate dominated builders have been used from the late 40's, but with increased environmental awareness and their implication in water pollution, their use has decreased in Europe and the United States, and have been replaced by Zeolites and polycarboxylic acids (Glennie, 2002). Through legislation or voluntary agreements, and the introduction of phosphate free detergents, several countries have implemented full or partial bans on the use of STPP in detergents. Italy and Belgium have implemented an almost total ban on STPP in detergents; Austria and Germany have restricted them. Some countries, Scandinavian, the Netherlands and Ireland rely on voluntary agreements with the producers. Only Greece, Luxemburg, Portugal and Spain have taken no actions, legislative or voluntary (CSTEE, 2003). The Irish Detergent Industry Association and the Irish Government signed an agreement to eliminate STPP in detergents on the Irish marketplace by 2002 (Glennie et al 2002).

3 Phosphorus Sources and the Phosphorus Cycle

Chapter Overview

In Chapter 3 the phosphorus cycle is introduced, and the impact of the various inputs of phosphorus into the environment are explained, with particular attention to anthropogenic eutrophication of aquatic systems, the cause and effects of increased phosphorus levels in an aquatic system.

3.1 Phosphorus Cycle

The phosphorus cycle begins in rocks. Phosphorus is weathered from the rocks and distributed in soils and water. Phosphorus changes type as it is cycled through the various reservoirs, from soluble to particulate, inorganic to organic.

The annual load of phosphorus to rivers from geological processes is extremely low (Mainstone et al 2000). Most phosphates in European aquatic systems is of an anthropogenic origin. Atmospheric deposition of phosphorus is estimated at 10kg/km^2/year, (Meybeck, 1982), and is not usually measured. As there is no stable gaseous phase, the phosphorus cycle is termed endogenic (Manahan, 2000).

Plants take up the inorganic phosphate ions from the soil, converting it to the organic form as they incorporate it into their tissues as nucleic acids, ATP, proteins and fats. Approximately 8 x10^{12} g P/year is mobilized from surface rocks and utilized by plants (Maybeck, 1982). The phosphates then moves from plants to animals as herbivores eat plants and carnivores eat plants or herbivores. The phosphates absorbed by animal tissue through consumption eventually returns to the soil through the excretion of urine and faeces, as well as from the final decomposition of plants and animals after death and remineralized.

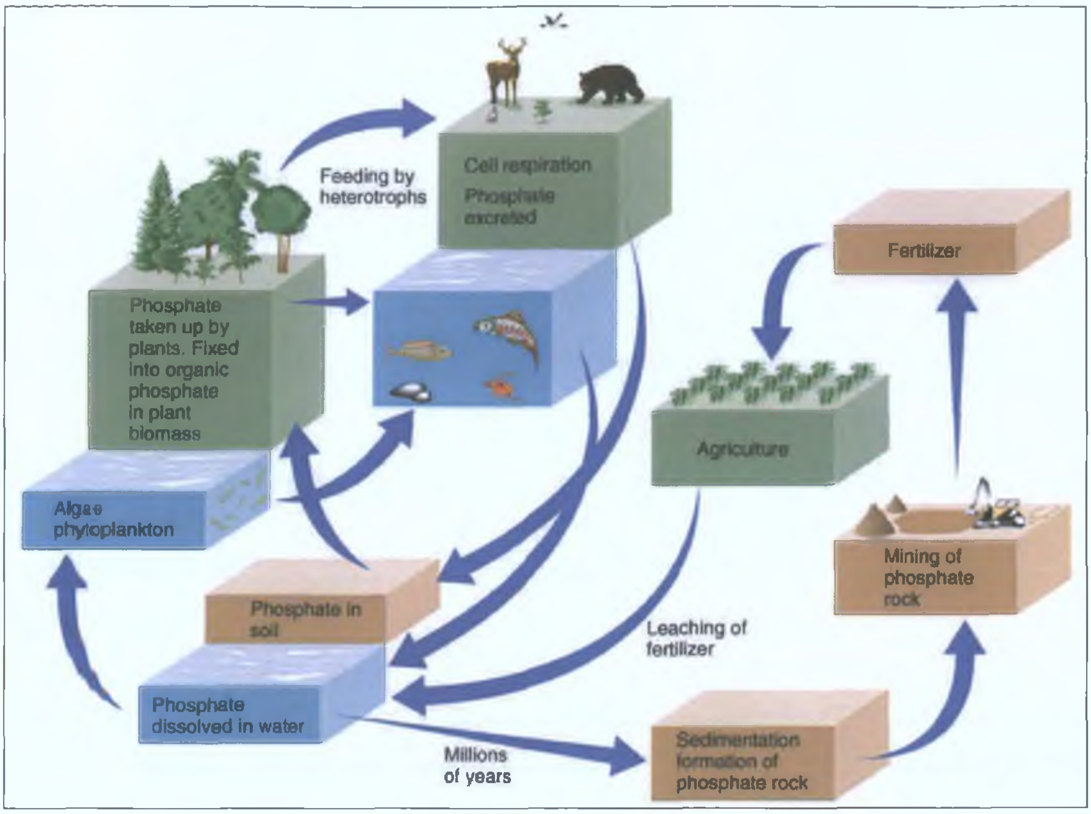


Figure 6. Phosphorus cycle. (Nebel & Wright, 2000)

3.2 Phosphorus in Aquatic Systems

Within the aquatic environment, Phosphorus is highly insoluble, binding tightly to molecules in soil, therefore it mostly reaches waters by traveling with runoff soil particles, or adsorbed to particulate matter. Phosphates can also enter waterways through fertilizer runoff, sewage seepage from septic tanks, natural mineral deposits, and wastes from other industrial processes. These phosphates tend to settle out as sediments on the river and lake beds. As sediments are stirred up, phosphates may reenter the phosphorus cycle. Aquatic algae and bacteria take up the phosphate which then travels up through successive stages of the aquatic food chain. River systems have an internal capacity to remove and/or release phosphorus from/to the water column to the sediments, as it cycles through the various inorganic, organic, particulate and soluble forms. House et al (1995) identify soluble reactive phosphorus (SRP) as the most abundant form of phosphorus in natural waters.

Glennie et al (2002) confusingly seems to include living biomass in his estimate, claiming organic phosphate is the dominant form in natural waters, retained in living and dead biomass, with about 30% as either soluble or particulate phosphorus , but agree that orthophosphate is the dominant bioavailable form. According to Glennie et al (2002) the majority of phosphorus enters natural waters in a non-bioavailable form, bound to suspended matter, and that only 5% is soluble.

Natural concentrations of total phosphorus and orthophosphate will vary from catchment to catchment, depending upon factors such as geology and soil type. Natural background concentrations vary from 0 to 10 μg P/l for orthophosphate and 5 to 50 μg P/l for total phosphorus. Levels above 500 μg P/l are considered as being of bad quality and significant eutrophication can be expected (EEA,2009).

SRP accounts for 52% of the TP in the River Sem and 80% of the TP in the East and West Avon (Jarvie et al 2005). SRP is the dominant phosphorus fraction (67%) in lowland rivers in the UK (Jarvie et al 2006). During summers, Molybdate reactive phosphorus (MRP) levels in a river slowly rise as flow decreases, reaching a peak before the first winter flows, when the MRP displays a rapid reversion to pre summer levels (Muscutt et al 1996). By definition, the difference between MRP and SRP is that SRP is filtered (usually on a 0.45μm filter. Refer to Chapter 7).

Phosphorus solubility is a function of pH and redox potential. Neutral pHs and aerobic conditions cause phosphorus to precipitate with metal hydroxides such as aluminum, iron and manganese. Under anaerobic conditions phosphorus is released from the sediments into the overlying water column when the iron and manganese precipitates dissolve. pH ranges either side of neutral can increase phosphorus release rates. Temperature also impacts on phosphorus release. A five fold increase in the rate of phosphorus release occurs between 2 and 25-35°C, with obvious implications for phosphorus release during summer when the water level is lowest (Kim et al 2003). While obviously beneficial for many biological processes, in surface waters an excessive concentration of phosphorus is considered a pollutant. In ecological terms, phosphorus is often a limiting nutrient in many environments; i.e. the availability of phosphorus governs the rate of growth of many organisms. Frequently over application of phosphorus to soils in excess of the crop requirement, causing excess fertilizer runoff increases phosphate levels in rivers and other bodies of water. According to Foy et al (1995), the accumulation of phosphorus in soil, rather than removal through crops and agricultural products is a feature of Western European fertilizer application.

4 Phosphorus and its impacts on the Environment

Chapter Overview

Chapter 4 explains the impact phosphorus on aquatic environments, with particular attention to anthropogenic point and diffuse eutrophication of aquatic systems, the contribution of each to eutrophication.

4.1 How Does Phosphorus get into water?

Other than natural geological weathering and natural processes, anthropogenic derived phosphorus can enter surface water from either point sources or non-point sources:

4.1.1 Point Sources:

Defined by the EEA (2005) as 'stationery locations or fixed facilities from which pollutants are discharged' and include:

- Municipal wastewater systems. Urban wastewater is one of the most important contributors to phosphorus discharges (EEA 2003). It is estimated that in 10 European Union states, containing 90% of the population, approximately 375,000 tonnes of phosphorus are produced in domestic wastewater each year, with up to 45% of this being removed by wastewater works (Farmer et al 2001).
- industrial discharges
- feedlots and manure piles.

4.1.2 Non-Point or diffuse Sources:

Defined by pollution from widespread activities with no specific point of discharge (EEA, 2005) and include:

- Atmospheric deposition, although such deposition of phosphorus is generally small
- erosion of soil from agricultural land, natural habitat and stream banks
- runoff water from agricultural land, and golf courses
- allowing livestock to graze along lakes and streams
- Septic tanks [Although in principal a point source, their abundance classes them as diffuse (EA, 2005)].

4.1.3 Relative Contributions

The relative importance of the phosphorus inputs is a function of anthropogenic pressures, land use, natural conditions, population density and connection to wastewater works and climate, and varies greatly between catchments. The sources differ in their phosphorus concentration, speciation and bioavailability (Withers, 2008). Point sources of phosphorus are more easily identified, quantified and controlled than diffuse sources (House et al 1997, Bowes et al 2005). In Ireland the EPA cites agriculture as the main culprit, as eutrophication is evident in areas without point soures (EPA, 1997). In the SWRBD, statistical estimates of the phosphate loading from diffuse sources is 817 Kg/day PO_4-P, with point sources at 86 Kg/day PO_4-P (SWRBD, 2008).

Relative estimates of the contribution by diffuse and point sources vary. CEEP (1999) estimate 33% of the phosphorus loading to surface waters in Europe is derived from sewage, for Ireland a lower value of approximately 16% is given and 50% from agriculture.

In Ireland, where diffuse agricultural discharges are the principal source of eutrophication in Irish lakes (DOEHLG, 1997), point sources' impacts may be proportionally greater than diffuse sources, as they enter the river throughout the year, and are at reduced dilution during the optimum growing season. The phosphorus from municipal wastewater treatment plants is highly bio-available as a significant amount is in the orthophosphate from. Phosphorus emanating from grassland may be 50% bioavailable, while phosphorus discharges contain a far greater percentage bioavailable phosphorus (EPA, 1997).

The phosphorus absorbed to particulate matter carried to waters during runoff events associated with winter and autumnal rains when the river is in spate contains proportionally less of the orthophosphate form, and the temperatures, light availability are less than spring and summer months. Much of this particulate matter is flushed out of the river system (Mainstone et al 2002).

Neal et al (2005) are in agreement, reporting 50% of the annual phosphorus loading to UK waters is now from agricultural wastes, but most significantly, the phosphorus concentration during vulnerable periods, i.e. low river flows, or base flow periods with low dilution and high biological activity is what governs ecological quality. Jarvie et al (2006), Muscatt et al (1996) agree, that it is the phosphorus concentration during the periods of greatest ecological sensitivity that determines the ecological quality of a river. During these periods, it is point source inputs that are the greatest source of bio-available phosphorus posing the greatest risk of eutrophication.

Groundwaters in Ireland are becoming increasingly contaminated with phosphates due to poorly sited and poorly managed septic tanks and other onsite smallscale treatment systems. During periods of low flow, up to 90% of the flow in a river can be attributed to base flow from the aquifer. Phosphate is now the main pollutant of Irish ground water rather than microbial pathogens or nitrate according to the classifications used by the Water Framework Directive (Daly et al 2009).

Garnier et al (2005) report point sources contribute three times as much phosphorus as diffuse sources in the Marne Basin, during a drier climate, whereas during a wetter climate, it was only 20% greater. In the Catalonia region of Spain, Marti et al (2004) estimate up to 89.2 ± 6% of the phosphate load being transported by an urban steam was contributed by WWTPs, with the WWTP discharge exceeding receiving waters discharge up to 77% of the time during summer months.

Discharges of phosphorus from point sources have decreased significantly during the past 30 years, whereas the loss from non-point sources has generally remained constant. As the impact of point sources becomes reduced, the impact of diffuse sources becomes proportionally greater (EEA, 2005).

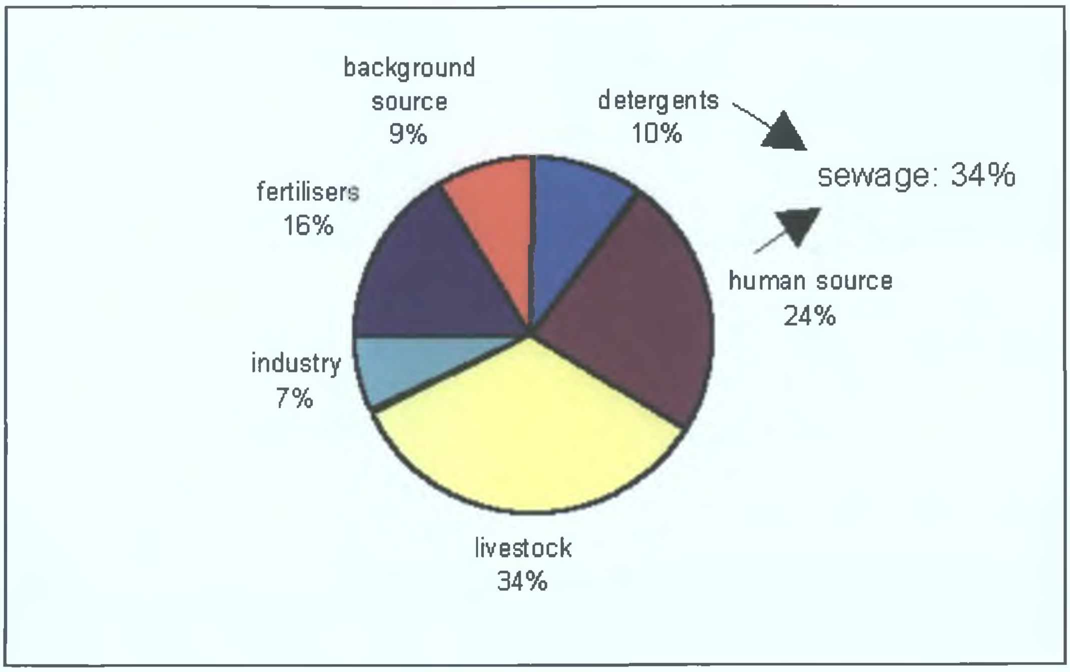


Figure 7. Phosphorus inputs into the aquatic environment in the EC. Imperial College of Science, Technology and Medicine, (1993)

The average agriculturally intensive European Country applies 8-13 Kg/ha of phosphorus to land (EEA, 2005). Smith et al (2001) report the losses of phosphorus from soil depends on the interval between application and runoff event, as well as rate and timing of manure application.

Studies of Lough Neagh (Foy et al 1995, Foy et al 2003) reported initial decreases in total phosphorus levels in the lake following tertiary treatment installation at major wastewater treatment plants in the catchment in late 1981. However by the 1990s the total phosphorus levels in the lake exceeded the 1981 levels. Increased diffuse loadings of phosphorus are cited as the cause of the increase. The internal storage capacity of sediments for phosphorus means it can potentially be available for re-release as soluble phosphorus after overlying water concentrations of soluble phosphorus have decreased substantially.

4.2 Eutrophication

Justus Von Liebig, a German agricultural chemist, published in the mid 1800's a series of books in which he proposed that the yield of a given plant species would be limited by the nutrient that is present in the lowest amount relative to the plants demands for growth, a concept now known as Leibig's Law of the Minimum.

In fresh waters, phosphorus is considered a key element in causing eutrophication in fresh waters. Nitrogen is often the limiting nutrient in saline waters. (OECD, 1982). The term "eutrophication" has its origins in the Greek word "eu" meaning "well" and trophos", meaning "nourished" (Tusseau-Vuillemin, 2001). But all-to-often, the term has come to be associated with adverse water quality. It is recognised by the European Commissions Scientific Committee on Toxicity, Ecotoxicity and the Environment (CSTEE) that excess phosphorus is responsible for eutrophication in inland waters, and besides oil pollution, eutrophication is the most important pollution problem in the Mediterranean Sea (CSTEE, 2003). Eutrophication is one of the most serious problems facing the ecology of the surface waters of the UK (Mainstone et al 2002), Ireland (EEA, 2005), Switzerland (Poté et al 2008), India (Krishnan et al 2007), Greece (Kagalou et al 2007).

The risk of eutrophication related to anthropogenic inputs is most significant when:
(a) The ecosystem can respond to the additional load with increase in algal productivity resulting in structural and functional changes; and
(b) Phosphorus is the limiting nutrient.

4.2.1 What is Eutrophication?

The UK Environment Agency defines eutrophication as "enrichment of waters by inorganic plant nutrients which result in the stimulation of an array of symptomatic changes. These include the increased production of algae and/or other aquatic plants affecting the quality of the water and disturbing the balance of organisms present within" (EA, 2003). Eutrophic areas are usually characterised by increased primary productivity and numbers of organisms, but with decreased biological diversity.

Almost all definitions of eutrophication imply a biological response to an increase in the amount of nutrients (Kelly et al 2004), whether it is due to nitrogen, silica or phosphorus. The estimated cost of damage to the environment in the UK due to anthropogenic induced eutrophication is between £75 and £114.4 million (Pretty et al 2001). Enrichment by inputs of phosphorus results in excessive production of cyanobacteria, algae and rooted plants. A healthy submerged plant community is imperative to the well being and ecological balance of a river. Submerged macrophytes provide valuable resources for a broad range of fauna, food, shelter, spawning substrate and breeding (Mainstone et al 2002).

Increased input of nutrients, particularly phosphorus can affect aquatic communities:

- Altering (usually reducing) species diversity by encouraging more competitive plants
- Enhance algal growth with resulting nocturnal oxygen sags during algal respiration (Mainstone et al 2000)
- Increasing siltation rates by trapping particulates and reducing rooting depth, making higher plants susceptible to being carried away by currents (Mainstone et al 2000)
- Reduced recreational aesthetics through reduced clarity and unpleasant odours.
- Loss/elimination of sensitive species (trout, salmon char) and their replacement with coarse fish (DOEHLG, 1997)
- Fish Kills; 5 Irish fish kills in 2004-2006 were attributable to eutrophication (Lucey, 2006)
- Phytotoxin production (USDA, 2003)
- Water treatment plant filter clogging (Garnier et al 2004).

Standing water bodies such as Lakes are generally more sensitive to nutrient inputs than other water bodies due to longer water retention time. Their sediments also act as sinks for nutrients compounding the problem. The eutrophication problem may be aggravated if the algal biomass sinking down out of the well oxygenated epilimnion and into the hypolimnion, where already oxygen depleted deeper waters attempts to cater for this new oxygen demand from decomposition of this new material. This algal oxygen demand, called secondary oxygen demand, may be 15 times higher than the original oxygen demand of the wastewater causing the algal growth (Källqvist et al 2002).

4.3 How best to eliminate eutrophication caused by phosphorus:

4.3.1 Diffuse Sources:

4.3.1.1 Septic Tanks

The contribution of septic tanks currently to phosphorus pollution is an estimation, and they are classed with diffuse sources. The Western River Basin District group are currently undertaking a major survey of the impact of onsite wastewater treatment systems (OSWTS) and septic tanks to determine the impact on groundwaters and surface waters and prioritise remedial works. Septic tanks cause problems where they are located on unsuitable land (poorly or too rapidly drained soils allowing inadequate percolation) or where there is a lack of maintenance and monitoring.

Personal experience shows there is little to no monitoring of such systems once permission has been obtained, unless there is a problem reported by a neighbour. Often the applicant just has to supply documentation, i.e. a quote from a treatment system supplier to support his application. There is no requirement to prove the system as proposed was actually installed or operated as proposed. Local Authorities currently do not have the resources to monitor these on site treatment systems, which represent a significant threat to ground waters and hence to surface waters.

Approximately 450,000 properties (31% of the national total) are currently unserviced by a public sewer, but rely on onsite treatment such as septic tanks or propriety systems, or no treatment. Traditionally, septic tanks were used to treat low volume, domestic wastewater. However, modern lifestyles with dishwashers, washing machines and power showers produce a hydraulic load in excess of what a septic tank can effectively treat. As septic tanks remove gross solids only, with 15-20% of the BOD loading, their ability to remove phosphorus is poor. The percolation area where the secondary treatment occurs is often overloaded. The lower densities of rural housing, lower volumes allowing a greater level of treatment within the septic tank meant that the problem of groundwater pollution was not as significant as today. An estimated 33% of the septic tanks (139,330) nationally are inadequate, up to 95% in some areas. With an estimated cost of remediating a site that is generally suitable at €7000/site to €20,000 for more difficult sites, it is estimated that between €975,310,000 to €3 billion would be required to remediate these septic tanks to a proper standard of treatment (ERM, 2007).

The current reference documents used in Ireland for the construction of septic tanks and on site wastewater treatment systems are both due to be replaced with the implementation of the European Communities Surface Water Quality Regulations . Both SR6: Septic Tank Systems: Recommendations for Domestic Effluent treatment and disposal from a single house and Environmental Protection Agency: Wastewater treatment Manuals: Treatment Systems for single Houses are due to be replaced in June 2009 by EN12566-Small wastewater treatment systems for up to 50 TP.

North Tipperary County Council are undertaking a pilot study “Waste Water Collection and Treatment for Rural Villages” investigating potential ways and costs of providing wastewater collection to small villages rural areas using innovative collection methods such as vacuum sewers, membrane based technologies, providing septic tank desludging services, and have estimated the cost at €25,000/house (ERM, 2007).

4.3.1.2 Agricultural Sources

With 17% of European soil being poorly drained, and agriculture the dominant use, reducing nutrient levels in overland flow through effective management will be difficult to achieve, particularly in a climate such as Ireland's. Artificial subsurface drainage, avoiding soil compaction, using weather forecasts to avoid spreading fertilizers during wet weather are effective management techniques of the reduction of the nutrient content of overland flow (Kurz et al 2005). According to Morse et al (1993) over 73% of phosphate inputs to Irish waters are of an agricultural origin, i.e. from livestock or fertilizers.

Agricultural controls should include:

- Use of vegetated buffer strips in the riparian zone
- Improved techniques for the application of fertilizers, including soil injection of organic wastes, or the use of slow release fertilizers
- Adequate storage of animal wastes
- Provision of water troughs removed from streams, rather than allowing the animals direct access to streams for drinking water.

4.3.2 Point Sources

4.3.2.1 Detergent Phosphate Bans

A ban in the use of phosphorus based detergents in Switzerland in 1986 coincided with an extensive phosphorus removal improvements at wastewater works. (Morse at al, 1993) saw significant reductions in the phosphorus concentrations in all major Swiss lakes as well as the river Rhine.

In Italy, a ban on the use of STPP in 1989 saw a 30% reduction in the phosphorus loading to the Adriatic, with a reduction in the amount of severe Eutrophication episodes. The contribution of this decline due to phosphorus removal at wastewater plants was considered negligible, as very few of them had phosphorus removal. Incidents of severe eutrophication have been significantly reduced (CSTEE, 2003).

There is also the argument from a sustainability perspective. Preventive intervention is preferable to treatment (CSTEE, 2003). Improving the quality while reducing the volume of wastewater to be treated is preferable to providing an end of pipe wastewater treatment plant. In line with "the polluter pays" principal, levies or charges should be structured that discharges with high concentrations of phosphate pay more than those discharging lower levels to the public sewer. Replacement of phosphate containing detergents would result in a reduction of load at source.

In contrast, a survey commissioned by CEEP of expert opinions on the impact of a change in the phosphorus concentration in influents (25-30% reduction) to a wastewater treatment plant concluded somewhat disingenuously that it would have little if no effect and might even impair existing biological phosphorus removal (Evans 2007). A reduction in the influent phosphorus load would affect how the wastewater treatment plant achieves compliance with its consent, i.e. a reduction in the amount of chemical dosing required. This may be of relevance to larger municipal wastewater plants >10,000 PE only, as these larger plants must comply with the 2mg/l limit as per the urban wastewater directive. Smaller plants, which are often situated in the more remote regions of a catchment and discharging to smaller streams, do not have to comply with this standard. Assuming 30 % of phosphorus is removed in a wastewater treatment works, a 25% reduction in the phosphorus load would result in 20% less phosphorus discharged in the effluent, a significant reduction. Such a reduction in phosphorus detergent would also improve the effect of diffuse septic tank inputs. Evans (2007) concedes that a reduction in the phosphate concentration of detergents would however reduce the total phosphorus load due to storm overflows, significant in an Irish context with the number of combined sewers and taking our climate into account.

A consideration in reducing phosphorus in influents may make EBPR viable for a greater number of plants as frequently the C:P ratio is too low for effective phosphorus removal.

4.3.2.2 Phosphorus removal at WWTPs

Increased use of phosphorus removal techniques at wastewater works will result in either increased volumes of sludges (if chemical precipitation is used) or increased phosphorus strength sludges (if EBPR used). Improper land application of these wastes will merely transform what was a controlled point discharge into an uncontrolled diffuse discharge. An effective management strategy will target all sources necessary to achieve the threshold levels.

Mainstone et al (2000) argue that although fairly immediate improvements in water quality were obvious after installing phosphorus removal at several English wastewater works, it could take some time before ecological improvements are observed owing to sediment phosphorus being recycled back into the water column.

Garnier et al (2005) report tertiary treatment at Colombes WWTP in Paris has reduced the phosphorus load to 0.2 g Phosphorus/person/day, and if this was further reduced to 0.15 g Phosphorus/person/day, it would lower the phosphorus loading on the Marne from 1260Kg Phosphorus/day to 200 Kg Phosphorus/day. Morse et al (1993) presents the interesting argument that implementing phosphorus removal at Irish wastewater treatment plants would be just 0.027 of gross domestic product (GDP) and 0.3% of tourism and leisure expenditure. As the effects of eutrophication are undesirable from a tourism and leisure perspective, a phosphorus removal strategy is surely justified.

The introduction of the Waste Water Discharge (Authorization) Regulations (S.I. No. 684 of 2007) will ensure Local Authorities do not allow new development to connect to already overloaded wastewater treatment plants

4.4 Summary

The Scottish Environmental Agency report reducing the phosphorus concentration in a lake by anything less than 20%, normally does not results in detectable changes in trophic status (SEPA, 2002), while Glennie et al (2002) suggest a phosphorus reduction of 70-90% is required before eutrophication and trophic status will improve.

Greatest ecological improvement in waters would be tackling the smaller scale wastewater treatment systems in upper, more sensitive, reaches of rivers, before tackling the large sewage treatment plants serving the population denser lowlands according to Jarvie (2006). Coupled with the designation of sensitive areas and application of tight emission limits for nutrients on wastewater effluents, a reduction in the phosphorus loading in influents through reductions/bans on the use of phosphorus in detergents. Commensurate with tacking the point discharges, tighter controls will be required on the use of phosphorus fertilizers, and the application to land of organic wastes.

The consensus is clear, Glennie et al (2002); Mainstone et al (2000); Morse et al (1993); CSTEE (2003); Balmer et al (1988): The greatest effect on reducing the phosphorus loading to waters would be designating the waters as sensitive, reducing the phosphorus discharge consent levels, and reducing the phosphorus levels of the influent through detergent phosphorus restrictions coupled with tackling diffuse inputs. Any water quality improvement strategy that doesn't embrace all, cannot eliminate eutrophic conditions.

Eutrophication is usually reversible, although the time taken to recover varies, from almost immediate to very long recovery times (Kagalou et al 2007). Rivers respond much faster to a reduction in loads than lakes, as they have greater oxygenation rates and flushing rates. According to Glennie et al (2002) oligiotrophic lakes respond slowly to an increase in nutrient inputs, and quickly to a decrease in load, while for eutrophic lakes the inverse is the case. Holmgren (1984) found lakes can recover within a year of ceasing artificial nutrient inputs, but Marsden (1989) found no change in trophic status over a 10 years period for some lakes.

5 Phosphorus and Irish and European Legislation

Chapter Overview

Chapter 5 outlines the principal pieces of European and Irish Legislation relevant to phosphorus discharges and the regulation thereof. Examples of planning application decisions appealed to An Bord Pleanala, where phosphorus in the receiving waters determined whether the developments went ahead are given as examples of the significance of phosphorus in an Irish context.

5.1 Water Quality Standards, Europe, Ireland and Phosphorus Legislation

The authoritative source for most water quality management policies and strategies regarding phosphorus is based on the Organisation for Economic Co-operation and Development (OECD) (1982) document 'Eutrophication of waters: monitoring assessment and control'.

The OECD with the support of its member countries (including Ireland) has established environmental indicators to inform society of the state of the environment. In 2001, the OECD established a shortlist of key indicators, one of which is "No. 5: Protection of freshwater quality indictors includes wastewater treatment connection rates and pollution loads to water bodies" (OECD, 2007).

A number of European Directives are in place which, inter alia, govern phosphorus limits for waters: EC Directives 76/1464 and 80/168/EEC both classify phosphorus as a List 2 substance, the discharge of which into the environment is to be controlled.

However, the primary legislative drivers for the control of phosphorus discharges into the aquatic environment in Ireland are

- The Urban Wastewater Directive (EC Directive 91/271/EEC)
- S.I No. 258 of 1998. Local Government (Water Pollution) Act, 1977 (Water Quality Standards for Phosphorus) Regulations, 1998) and
- The Urban Wastewater Directive, and the European Unions Water Framework Directive (2000/60 EC).

EC Directive 75/440/EEC transposed in Ireland by European Communities (Quality of Surface Water Intended for the Abstraction of Drinking Water) Regulations (S.I. No. 294/1989), specify two standards for soluble reactive phosphorus as guideline values: 0.5mg/l for A1 waters, and 0.7mg/l for A2 and A3 waters. Although given the purpose of the Directive, these values are intended for protection of human health rather than an environmental objective.

In July 2007, the EPA published a discussion document for public consultation on proposed new quality standards for surface water classification. Driven by the Water Framework Directive, it is proposed that where waters are in danger of failing to meet their objective of achieving “good status” (refer to section 5.3), a programme of measures specified in the river basin management plan will be put in place to ensure achievement of the target “good status” . Trigger Action Values (TAVs) are proposed for certain physio-chemical parameters such as phosphorus. TAVs are to be used in conjunction with environmental quality standards (EQSs), but will provide a more stringent non-binding target than the EQS. Exceeding a TAV would prompt investigation and action, exceeding the EQS criteria would be an actual offence.

Table 2. Proposed TAVs for Phosphorus

Nutrient Conditions	Rivers	Lakes	Transitional	Coastal
Molybdate Reactive Phosphorus (MRP)	TAV High/Good boundary <16µg P/l TAV good/moderate Boundary <30 µg P/l EQS High/Good Boundary <34 µg P/l EQS Good/Moderate Boundary <50 µg P/l (Median)		0-17psu (Winter Median) EQS 60 µg P/l 35psu (winter median) EQS 40 µg P/l	
Total Phosphorus		T.B.C		

In September 2008, Draft European Communities Environmental Objectives (Surface Waters) Regulations were published, which proposed two classifications for water, 'high status' and 'good status'. ≤ 0.025mg/l (mean) or ≤0.045 mg/ (95%ile) and ≤ 0.035 mg/ (mean) or ≤ 0.075 mg/ (95%ile) mg/l as MRP, respectively with three classifications for water bodies defined:

'High Status'

There are no, or only very minor anthropogenic alterations to the values of the physio-chemical and hydromorphological quality elements for the surface water body type from those normally associated with that type under undisturbed conditions. The values of the biological quality elements for the surface water body reflect those normally associated with that type under undisturbed conditions, and show no, or only very minor, evidence of distortion.

‘Good Status’

The values of the biological quality elements for the surface water body type show low levels of distortion resulting from human activity, but deviate only slightly from those normally associated with the surface water body type under undisturbed conditions.

‘Moderate Status’

The values of the biological quality elements for the surface water body type deviate moderately from those normally associated with the surface water body type under undisturbed conditions. The values show moderate signs of distortion resulting from human activity and are significantly more disturbed than under conditions of good status. Surface waters achieving a status below moderate shall be classified as poor or bad.

For river water bodies, the quality elements to be taken into account include composition and abundance of aquatic flora, composition and abundance of benthic invertebrate fauna, and composition abundance and age structure of fish fauna. Composition, abundance and biomass of phytoplankton are also included for lakes, transitional and coastal water bodies.

Previously environmental quality standards applied to waters specifically designated for the protection of fish (i.e. Statutory Instruments: S.I. No. 293/1988. European Communities (Quality of Salmonid Waters) Regulations, 1988). These new regulations will see the environmental quality standards applied to all waters.

5.2 Local Government (Water Pollution) Act, 1977; (Water Quality Standards for Phosphorus) Regulations, 1998) S.I. No. 258 of 1998.

In 1997, the Irish Government published a strategy document "Managing Ireland's Rivers and Lakes - A Catchment Based Strategy against Eutrophication". The document set out Ireland's phosphorus reduction programme and laid down interim quality standards over a ten-year timeframe. The long-term target was to improve all polluted rivers and lakes to a level consistent with the beneficial uses of their waters. Transcribed into Irish Law in 1998 as Local Government (Water Pollution) Act, 1977 (Water Quality Standards for Phosphorus) Regulations, 1998. Targets based on phosphorus concentrations or biological quality (known as Q values) were to be met by 2007, although there was provision for an extension of this deadline to 2013 for difficult sites.

Median Molybdate Reactive Phosphorus values or biological quality ratings are to be used in determining the water quality of rivers, while total phosphorus or trophic status based on chlorophyll concentrations are to be used for lakes. At the time, the regulations were unique in Europe in that they included a biological assessment of eutrophication (Lucey et al 1999). Essentially, a Local Authority must ensure that where water quality is satisfactory it must be maintained, and where unsatisfactory, it must be improved. Through programmes based on improving local agricultural activities such as organic waste storage and disposal, silvicultural practises such as fertilization, and improving the quality and monitoring of municipal and industrial wastewater discharges, Local Authorities, hope to achieve compliance by the prescribed date.

The following table No. 3 shows the interim target levels to be achieved by Irish rivers by 2007 to ensure compliance with the regulations. As can be seen 30 µg/l molybdate reactive phosphorus (MRP) is the threshold between polluted and unpolluted water.

Table No. 4 shows the interim target levels to be achieved by Irish lakes. Total phosphorus concentrations are to be used for lakes.

Table 3. Water Quality targets for Rivers

If	**Then**	
The existing Q value falls into the category below;	**Either** the minimum Q-Value to be achieved is;	**Or** the median molybdate reactive phosphate (μg/l P) concentration to be achieved is
Unpolluted / Satisfactory water quality)		
5	5	15
4-5	4-5	20
4	4	30
Polluted/unsatisfactory water quality		
3-4	4	30
3	3-4	50
2-3	3	70
<2	3	70

Table 4. Water Quality targets for Lakes

If	**Then**	
The existing Trophic status is	**Either** the minimum target trophic status to be achieved is	**Or** the average total phosphorus concentration (μg/l P) to be achieved is
Unpolluted / (Satisfactory water quality)		
• Ultra-Oligiotrophic	Ultra-Oligiotrophic	<5
• Oligiotrophic	Oligiotrophic	>5 <10
• Mesotrophic	Mesotrophic	>10 <20
Polluted/unsatisfactory water quality		
• Eutrophic (moderately, strongly, highly)	Mesotrophic	>10 <20
• Hypertrophic	Eutrophic	>20 <50

Should water quality deteriorate from a Q5 status to a Q4-5, the site will be deemed noncompliant with the regulations, even though the water quality remains satisfactory. A

Q3 site that remains a Q3 site by the 2007 deadline would be deemed non compliant and unsatisfactory as it has not achieved its water quality target of improvement. Compliance depends on the better of the two, either biological water quality or MRP levels (EPA, 2005).

The land use at the majority of the Q5 and Q4 sites which have demonstrated deterioration in water quality is agriculture followed by forestry (Cork Co. Co., 2006). Agriculture is recognized at both a national level and within the County as being a major influence on eutrophication, with rural housing developments an emerging pressure. With the rezoning of former agricultural land for housing, significant pressures are now being placed on already overloaded municipal wastewater treatment plants, with developers proposing small scale treatment plants to serve their developments. Neal et al (2008) report a similar problem in England, with increased water abstraction rates to provide potable water for the developments compounding the problem by lowering the levels in the receiving waters. Article 43 of the Wastewater Discharge (Authorization) Regulations 2007 (S.I. No. 684 of 2007) makes it a requirement that a Sanitary Authority consider the effect of adding additional loading to a wastewater treatment works, and the effect of this additional loading on the receiving waters.

The population of the 170 catchments in Ireland is expected to increase by around 36% from approximately 1.2 M in 2002 to 1.6 M in 2022, with receiving waters' phosphorus assimilative capacity already limited in 78% of the sites surveyed (DoEHLG, 2005).

5.2.2 Phosphorus Regulations and Planning Permission Applications

The 2006 Cork County Council Implementation Report addressed the fact that there is currently confusion in the calculation of assimilative flows, with clarity required as to whether 95 percentile, average or median flows should be used in determining median phosphorus targets (Reynolds, 2006).

In a 2005 a decision by Meath County Council to refuse a discharge license to a housing development was appealed to An Bórd Pleanalà by the developer Noonan Construction Ltd. The use of the 95 %ile flow used by Meath County Council was challenged by the Appellant, who claimed using the average flow, the impact of the discharge would be lower, with 105 µg/l (Noonan) versus 156 µg/l (Meath Co. Co). However both parties were in agreement there was no assimilative capacity in the receiving waters! (Noonan Construction Ltd. V. Meath County Council 2005). Council's decision to refuse was upheld by An Bórd Pleanalá (WW.0295, 2005).

Other contentious planning cases where the effect of phosphorus on the local aquatic systems due to the development include:

Nora McCarthy V. Cork County Council

Cork County Council's decision to grant permission for residential development including a 900 PE wastewater treatment plant was appealed successfully by a third party on the grounds there was insufficient phosphate assimilative capacity in the proposed receiving waters. Although the developer proposed connecting existing unsewered dwellings, inspections of local agricultural practises by Cork County Council should have improved phosphate levels, these were insufficient to satisfy the board that existing elevated phosphate levels would not be exacerbated. (An Bord Pleanalá, 2006) PL 04.216991, 2006).

E.R.F.B V. W.C.C

Wexford County Council's decision to grant a Section 4 Water Pollution discharge licence for a small residential development with communal wastewater treatment plant and outfall to waters was appealed by the Eastern Regional Fisheries Board. The appeal was upheld by An Bórd Pleanalá due to the likely increase in phosphorus levels in the receiving waters (26.WW.0334, 2007).

E.R.F.B V. W.C.C

Wexford County Council's decision to grant Section 4 discharge licences to two single dwellings discharging to a small stream was challenged by the Eastern Fisheries Board. The challenge was upheld by An Bord Pleanalá (26.WW.0355, and 26.WW.0340, 2007) on grounds of insufficient assimilative capacity in receiving waters [some County Councils currently have an unwritten policy not to entertain applications for single dwellings discharging to surface waters].

Curraghboy Residents Group V. R.C.C

Roscommon County Council's decision to grant planning permission for the construction of a sewage treatment plant to serve a residential development at Curraghboy, County Roscommon was appealed by Curraghboy Residents Group. Appeal upheld by An Bórd Pleanalá on grounds of insufficient assimilative capacity in the receiving waters (PL20.229036, 2008).

5.2.2 Water Quality in County Cork

Water quality in Cork County is generally good, with a relatively high level of compliance. An improvement in the number of stations with satisfactory water quality was reported, from 77.4% during the baseline survey to 81.1 % in 2001-2003 (EPA, 2005).

However, there are two major concerns, a decline in the number of the sites with the highest biological quality from 123 to 93 sites, and a rise in the level of seriously polluted stations. In some cases it is not immediate obvious what the culprit is, although for the polluted stations, agriculture pressures are believed responsible. Reflecting the agricultural use of the county, 75% of the land use in the SWRBD is agricultural (SWRBD, 2007), the level of compliance for lakes, is 7 out of 24 non compliant (EPA, 2005). This decline in the number of highest quality sites is reflected at a national level, down from 4.6% of the baseline stations to 2.7% in 2001 - 2003 (EPA, 2005). These highest quality sites are usually found where there are little catchment pressures, and are most often found in the upper reaches of a river system.

Concurrent to the decline in highest quality water, there is also a decline in the amount of seriously polluted rivers. The reduction in the percentage of seriously polluted rivers is generally attributed to better sewage treatment plant performance (Toner et al 2005). Currently, approximately 69.5% of the national monitoring stations are compliant with the regulations for the period 2004-2006, up 6.1% from the period 2001-2003. As of 2006, 7.14% of Irish rivers are unpolluted, with 0.6% seriously polluted. With regard to lake quality, for the reporting period 2004-2006, 85.3% are oligiotrophic/ mesotrophic, and 3.3% are Hypertrophic (Lucey, 2006).

5.3 The Water Framework Directive

The 2000 European Unions Water Framework Directive (2000/60EC), transposed into Irish law as the European Communities (Water Policy) Regulations (Ireland) (S.I 722 of 2003) requires the integrated management of all water resources at a catchment or river basin level throughout the union from 2002 on. The objective is to achieve "good status" or "maintain good status" by 2015. According to the UK Environment Agency, "It is the most important new European water legislation to emerge for decades."

Currently 28.6% of Irish waters do not meet this objective. The main threat in Ireland is due to excessive nutrient loading, particularly phosphorus and nitrogen, to waters causing eutrophication (ERM, 2007). The Directive provides new impetus for the control of phosphorus and other pollutants, and focuses on priority areas, particularly SACs (Special Areas of Conservation) and designated sensitive areas under the Urban Wastewater Treatment Directive. The WFD introduces objectives and management which aim to create a "win-win situation between ecology and economy" (Commission of the European Communities 2007).

The objectives of the WFD are:

- to protect and enhance the status of aquatic ecosystems (and terrestrial ecosystems and wetlands directly dependent on aquatic ecosystems)
- to promote sustainable water use based on long-term protection of available water resources
- to provide for sufficient supply of good quality surface water and groundwater as needed for sustainable, balanced and equitable water use
- to provide for enhanced protection and improvement of the aquatic environment by reducing / phasing out of discharges, emissions and losses of priority substances
- to contribute to mitigating the effects of floods and droughts
- to establish a register of 'protected areas' e.g. areas designated for protection of habitats or species.

To achieve the objectives of the WFD, member states must identify, divide and characterise their waterbodies into River Basins, and identify the principal pressures acting on each waterbody. These RBDs serve as administrative areas for a co-ordinated approach to water management. In Ireland Local Authorities are required to co-ordinate their water management actions in each RBD. A monitoring programme of all water bodies within the basin must be implemented. Each river basin must produce a River Basin Management Plan (RBMP) which will include a programme of measures to achieve the WFD objectives. Public consultation is a key component among those specified in the formulation of the River Basin Management Plan by the regulation transposing the WFD into Irish Law. As can be seen from the table below, RBMPs are not due until 2009.

Using the above action deadlines as indicators, Ireland’s performance to date compares very favourably relative to our European neighbours, with the highest level of compliance for administrative set up. Ireland also scored highly on the economic and environmental analysis:

Table 5. WFD. Schedule of Implementation.

Deadline	Action Required
2000	Directive entered into force
2003	Transposition into national legislation
	Identification of River Basin Districts and Authorities
2004	Characterisation of river basin: pressures, impacts and economic analysis
2006	Establishment of monitoring network
	Start public consultation
2008	Present draft River Basin Management Plans to public
2009	Finalise river basin management plan including programme of measures
2010	Introduce water pricing policies
2012	Make operational programme of measures
2015	Meet environmental objectives, first management cycle ends
2021	Second management cycle ends
2027	Third management cycle ends and last extension of deadlines ends

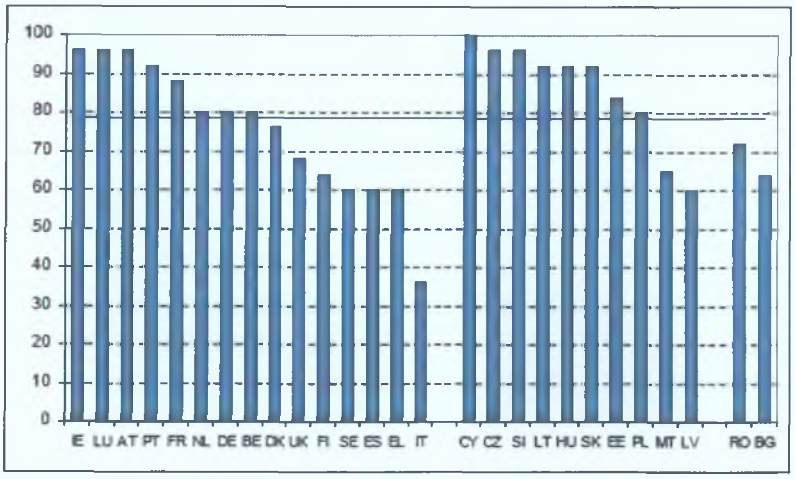


Figure 8. WFD Article 3-performance indicators. (Commission of the European Communities, 2007)

Ireland is divided into eight RBDs as shown in Fig.9. Four of these are in Ireland, (South East RBD, South West RBD, Western RBD and the Eastern RBD), one in Northern Ireland (North East RBD) while three are International RBDs (Shannon IRBD, North West

IRBD and the Neagh-Bann IRBD). County Cork is located almost entirely in the SWRBD as shown in Fig10, along with parts of Counties Limerick, Kerry, Waterford, South Tipperary as well as Cork City.

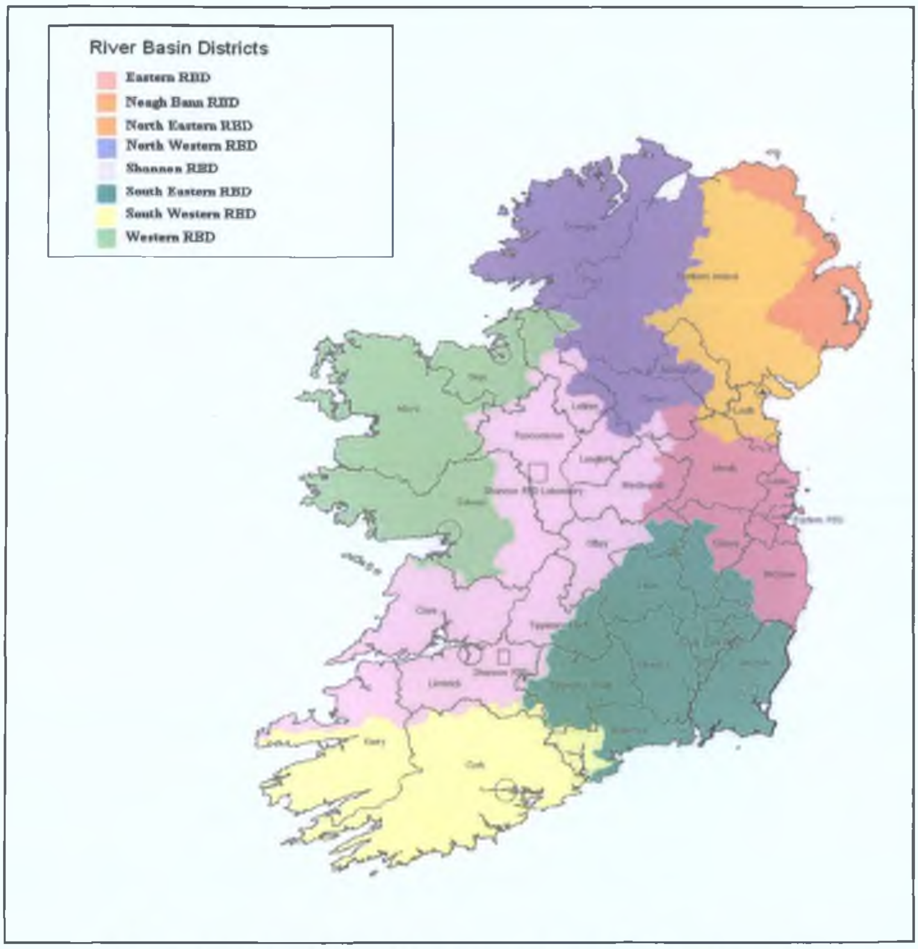


Figure 9. Irelands River Basin Districts (www.wfdireland.ie)

Figure 10. South West River Basin District. (www.swrbd.ie)

5.4 EC Directive 91/271/EEC (Urban Wastewater Directive)

5.4.1 UWWD Targets

The 1991 Urban Wastewater Directive requires sewage collection systems to be established as well as setting standards for sewage treatment for agglomerations over 2,000 population equivalents (PE). Either emission limit values or percentage reduction are provisioned for. For agglomerations smaller than 2000PE, there must be an 'appropriate' level of treatment provided, meaning the discharge must allow the receiving waters to meet relevant quality objectives.

It is expected that implementation of the directive will result in improved standards of wastewater treatment by:

- 50% reduction in the population not connected to sewers
- Elimination of untreated discharges of wastewater
- Most wastewater receiving at least secondary treatment
- 45% of municipal wastewater receiving nutrient removal
- Secondary treatment will predominate in Ireland, the UK, Portugal, Spain Italy and Belgium
- Tertiary treatment will predominate in Austria, Germany, France, Luxembourg, the Netherlands, Finland and Sweden Farmer(1999).

2005 was the deadline for full technical implementation of the directive (See Table No. 6) although countries are varying considerably in their success rates. Its requirement for phased improvement in wastewater treatment and nutrient removal for certain wastewater discharges depend upon the population equivalent and on the receiving waters.

Table 6. UWWD Implementation Schedule.

	December 1998	December 2000	December 2005
Sewage collection	> 10,000 PE in sensitive areas.	>10,000 PE in normal areas	>2,000 PE in all areas
Primary or secondary treatment		>15,000 PE in less sensitive areas	>10,000 PE in less sensitive areas
Secondary treatment		>15,000 PE in normal areas	>2,000 in normal and sensitive areas.
More advanced treatment	> 10,000 PE in sensitive areas		

More stringent measures are required for agglomerations discharging to 'sensitive' areas. The three criteria by which an area must be designated sensitive are:

- Freshwater bodies, transition and coastal waters which are eutrophic, or at risk of eutrophication
- Surface waters with more than 50mg/l nitrates from which drinking water is abstracted
- Areas where further treatment is required to comply with other EU directives.

Member states are required to review areas designated as sensitive at least every four years.

5.4.2 UWWD Implementation

How countries implemented the directive varied considerably. Some countries, Denmark and the Netherlands, declared the whole territory as sensitive (EEA, 2007). Generally, 'mainland' Europe has taken a much stricter stance phosphorus control, and designated a greater number of sensitive areas. The entire territory of Denmark, Netherlands, Sweden and Finland, as well as a large proportion of France and Germany have been designated sensitive areas (Mainstone et al 2002).

A standard of phosphorus removal to less than 2mg/l of Total Phosphorus for plants greater than 10,000 P.E and 1mg/l for plants greater than 100,000 P.E, or an 80% reduction in influent concentration is required for plants discharging to designated sensitive waters (See table 7). Nutrient reduction required for discharges to specified sensitive waters, have been provided for all Irish agglomerations specified by the regulations (EPA, 2007). Ireland, in transposing the directive in Irish legislation in the Urban Wastewater Treatment Regulations (S.I. 254/2001) designated 18 rivers, 6 lakes and 14 estuaries as sensitive areas. Sections of two rivers were designated in Cork, the River Bandon, and the River Blackwater. The 2004 Amendment (S.I 440/2004) designated two further areas in Cork as sensitive, both in Cork Harbour. Cork's sensitive areas are shown in Fig.11.

Table 7. UWWD ELVs for TP and TN

Parameters	Concentration	Minimum % of Reduction
Total Phosphorus	**Option 1**	**Option 3**
	2mg/l P	80%
	10,000-100,000 PE	
	1mg/l P	
	>100,000 PE	
Total Nitrogen	**Option 2**	**Option 4**
	15mg/l N	70-80%
	10,000 -100,000 PE	
	10mg/l N	
	>100,000 PE	

Figure 11. Designated sensitive waters in SWRBD. (www.swrbd.ie)

The UK through S.I 2841 of 1994 The Urban Wastewater Treatment Regulations designated 92 areas as sensitive in 2001. Wastewater treatment plants greater than 2000 PE discharging to sensitive waters will require phosphorus removal. With approximately 2000 plants in the UK above 2000PE, it is estimated the installation of nutrient stripping at these works will cost £13 billion (Select Committee on the Environment, Transport and the Regions, 1998).

A European Court of Auditors report in 1998 found "most of the member states were finding (meeting the requirements for sensitive areas) difficult to achieve... within the specified time frame" (CEEP, 1999). Overall the European Environment Agency report considerable progress, as well as "deplorable shortcomings" among the member states (EEA, 2007). Reasons cited for member states failing to achieve the targets include lack of economic incentives to promote eco-efficiency, inadequate funding, poor connectivity rates to wastewater treatment facilities, lack of co-ordination between public agencies (EEA, 2005).

Nordic and Western countries have the highest levels of tertiary treatment, while Southern Europe and the Accession countries have the lowest levels due to the earlier implementation of policies to reduce eutrophication and improve the quality of bathing waters EEA (2004) in the Nordic and Western countries. Norway's wastewater treatment plants are designed for optimum phosphorus removal rather than BOD/SS removal, and some reconstruction will be required to comply with the organic matter removal requirement (Källqvist et al 2002). Countries such as Ireland, Belgium and the Accession Countries have a relatively low percentage of their population connected to wastewater treatment (European Agency, 2003). In Ireland, 11% of waste water arisings received no treatment, and another 5% receive only preliminary treatment (EPA, 2007).

Further phosphorus reductions have been reported due to the transitional economies of some Accession Countries with the closure of several potentially polluting industries and a decrease in agricultural fertilizer use (EEA, 2004).

The UWWD has been cited as the reason for a steady decrease in the concentration of orthophosphate in European rivers over the last 10 years (EEA 2004), Fig No. 12 below).

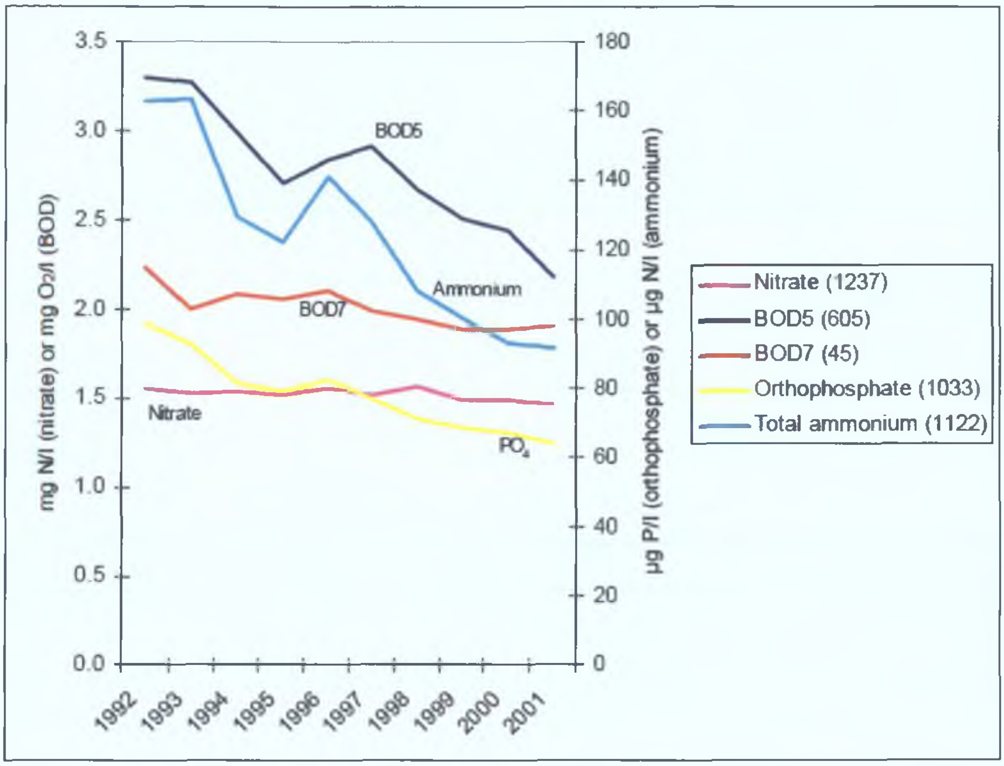


Figure 12. Declining nutrient levels in European Rivers (EEA, 2005)

5.4.3 Ireland and UWWD compliance

The percentage of Irish urban waste water receiving secondary treatment has increased significantly from 26% in 1998-1999 to 82% in the 2004-2005 period. (See Fig No. 13 below) mainly due to the major wastewater treatment infrastructure at Ringsend (Dublin), Carrigrennan (Cork) Mutton Island (Galway), Mungret (Limerick) and Dundalk. 12% of wastewater arisings now receive nutrient reduction following secondary treatment, up from 8% in 2000/2001 and 9% in 2002/2003 (EPA, 2007).

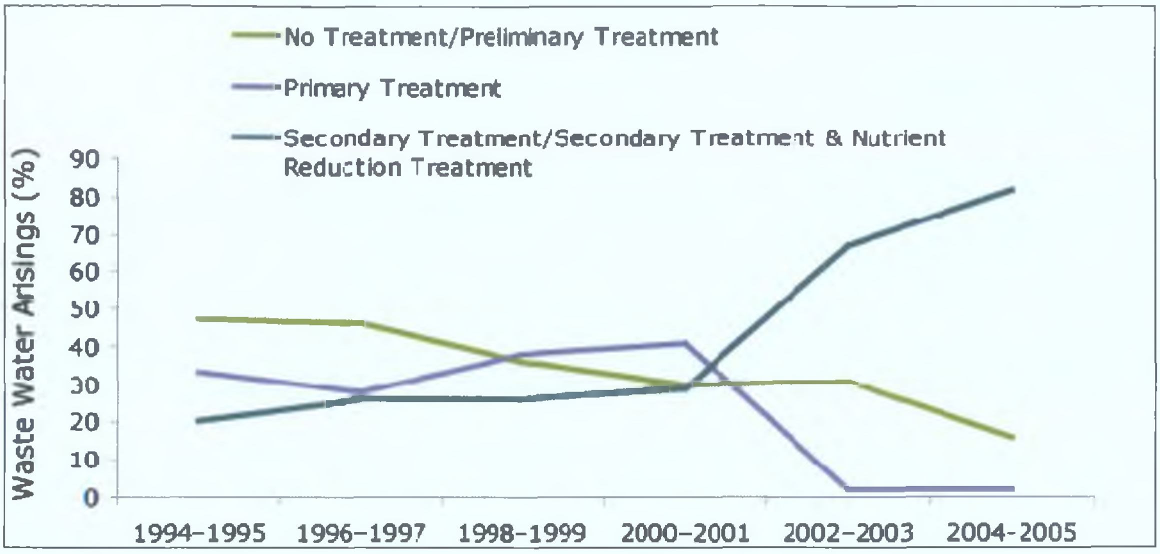


Figure 13. Improvements in Urban Wastewater Treatment in Ireland 1994-2005 (EPA, 2007)

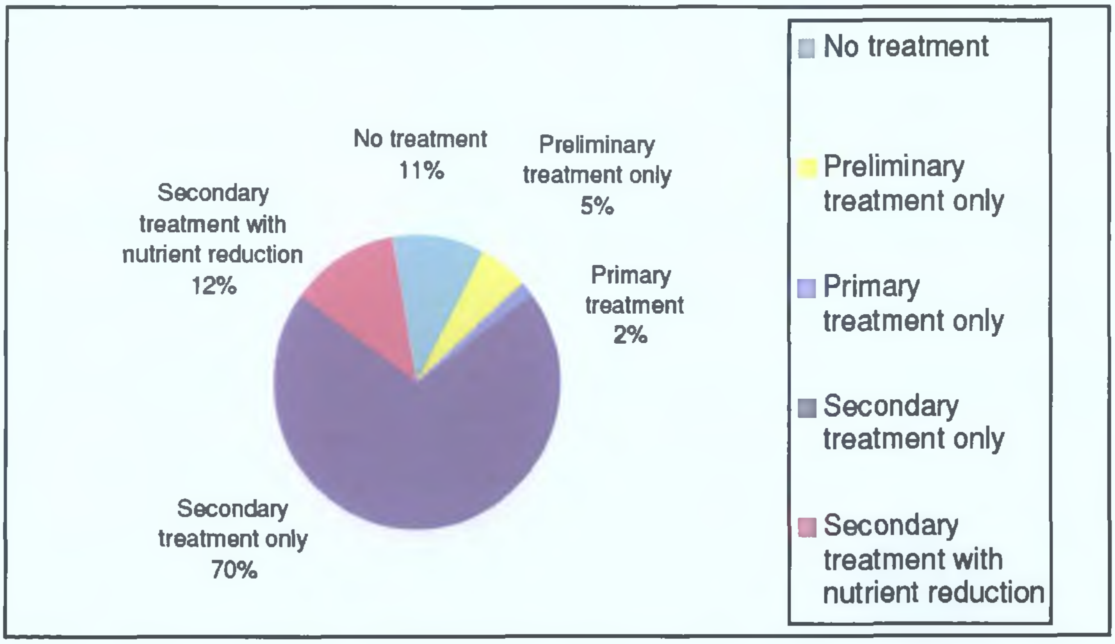


Figure 14. Wastewater facilities for agglomerations >500PE. (EPA, 2007).

The 2006 census identified the sewage facilities provided nationally to households. It should be noted that the connection to a public scheme may not necessarily mean any treatment is provided. The Irish government's stated aim is to provide secondary waste water treatment plants for all agglomerations with a population equivalent of greater than 1,000 (DoEHLG, 2005).

Table 8. Type of Sewerage Facilities on a National Basis (ERM, 2007)

Type of Sewerage Facility	Number of Private Households	% overall
Public Scheme	956,239	65.4
Individual Septic tank	418,033	28.6
Individual treatment system	29,685	2
Other	6,979	0.5
None	4,179	0.3
Not stated	47,181	3.2
Total	1,462,296	

5.5 Waste Water Discharge (Authorization) Regulations 2007 (S.I. No. 684 of 2007)

In September 2007, the Waste Water Discharge (Authorization) Regulations 2007 (S.I. No. 684 of 2007) were implemented to provide for the authorization by the EPA of urban waste water discharges by local authorities and for the purpose of giving further effect to provisions of Council Directive 76/464/EEC (the Dangerous Substances Directive) on pollution caused by certain dangerous substances discharged into the aquatic environment of the Community and Council Directive 2000/60/EC (Water Framework Directive).

The regulations phased in the authorization of WWTPs, based on a PE size. The first tranche of plants >10,000 P.E is currently in the licensing phase, with applications submitted in December 2007. The next tranche, 2000 – 9999 P.E applications were submitted in September 2008, with plants 1000 – 1999 due the following February 2009. The EPA’s stated aim of the regulations is to ensure through stringent conditions on the operation of such discharges, the achievement of good surface water and ground water status in addition to complying with standards and objectives established for associated protected areas by 2015 at the latest (EPA, 2007).

6 Wastewater Treatment and Phosphorus Removal

Chapter Overview

Chapter 6 discusses common wastewater treatment techniques with particular attention to the various physical, chemical and biological removal/reduction mechanisms for phosphorus. The type and relative amount of each type of phosphorus encountered in wastewater are explained.

6.1 Phosphorus in wastewaters

Phosphorus exists in three main forms in wastewater;

1. Ortho-phosphates or inorganic phosphates, with the chemical formulae; PO_4^{3-}, HPO_4^{2-}, $H_2PO_4^-$ and H_3PO_4 (orthophosphoric acid). Orthophosphates are available for biological metabolism without further breakdown, and are known as 'readily bioavailable'.

2. Condensed inorganic phosphates, also know as hydrolysable phosphates. These can be linear chain bonded polyphosphates or cyclic bonded meta-phosphates. Polyphosphates are phosphate molecules with two or more phosphorus atoms, oxygen atoms and sometimes hydrogen atoms. The simplest polyphosphate, pyrophosphate ($P_2O_7^{4-}$), is produced by the condensation or polymerization of two orthophosphate molecules.

$$2PO_4^{3-} + H_2O \rightarrow P_2O_7^{4-} + 2OH^- \qquad \text{Eqn 7}$$

Other polyphosphates include triphosphate $P_3O_{10}^{5-}$, which with sodium, is one of the main phosphate constituents of detergents as STPP (refer to section 2.6) Polyphosphates hydrolyze and revert to the orthophosphate form. Algae and other microorganisms are reported to catalyze the hydrolysis (Manahan, 2000).

Polyphosphates are constituents of some detergents and water softeners and are the most common condensed phosphate in urban wastewater.

3. Organic phosphorus e.g. Phospholipids, sugar phosphates, organo-phosphorus pesticides, nucleic acids.

All these phosphorus forms can exist as soluble, or attached to particulate matter.

6.1.1 Amount of phosphorus in wastewater

In Ireland, according to the EPA (2000), the average total phosphorus content of raw domestic wastewater from a single dwelling is 10 mg/l. Alexander & Stevens (1976) report the total per capita phosphorus value (discharge) as 1.8 g P/cap/d from a Northern Ireland city. Smith et al (2005) estimate 2.1g P/person/day or 0.766 Kg total phosphorus/person/year. CEEP (2008) give 2.4g P/person/day or 2.6g P/person/day including storm tanks in the UK. Metcalf & Eddy (2003) compared g/person/day total phosphorus for various countries. Ranging from 0.4-0.6 g/person/day TP for Uganda, 1.2-1.6 g/person/day for Germany to 2.7-4.5 g/person/day TP for the United Sates.

Foy et al (1995) apportion total phosphorus loading per person as: 47.8% due to dietary phosphorus, 42.4% from detergent, and 9.8% from dishwasher contribution. CEEP (1999) estimate the each person in the EU produces about 0.7Kg Phosphorus/year, 50% of which is ‘available’. The differing values arise when detergent phosphorus is included. A figure of 1.5-1.6 g P is generally accepted for Europe, with approximately 1% of dietary phosphorus retained in the body, approximately 66% of the waste phosphorus is excreted in urine, and 33% egested in faeces (CEEP, 2008). Halliwell et al (2000) found that detergent phosphate can range from 260g P/day on “low washing days” to 355g P/day, or “high washing days” (Saturday, Monday and Wednesday).
The European Environment Agency report total phosphorus loadings per capita in industrial countries between 1.0 and 1.5 Kg total phosphorus/person/year (Smith et al 2005). Other authors report similar levels. Lie et al (1997) report total phosphorus levels

of 5.7mg/l in influent entering Öresundsverket wastewater treatment plant in Helsingbog, Sweden. Prochaska et al (2006) report levels between 6 – 10 mg/l total phosphorus, Akay et al (1998) report 10mg/l total phosphorus in a raw sewage influent.

With the introduction of household detergents in the late 1940s and early 1950s the phosphorus produced per person doubled from approx 0.4 kg Phosphorus/Person/year to approximately 0.8 Kg Phosphorus/Person/year by the 1970's, and by the 1980's it reached 1.0 Kg Phosphorus/person/Year. By 1998 however, per capita levels were down to the 1968 level of 0.75 Kg Phosphorus/Person/year (Foy et al 2003).

Current estimates of the typical discharge of phosphorus per person/year has dropped from 0.7-0.8 kg Phosphorus/year/person to approximately 0.05 – 0.2 kg Phosphorus/person/year (CEEP 1999).

A very important consideration in discussing phosphorus concentrations in domestic wastewaters and urban wastewaters in the amount of dilution by clean water, either through infiltration by ground water into the foul sewer, or from rainwater in combined sewers.

6.2 Phosphorus species in sewage

Dueñas et al (2002) found strong correlation between influent soluble phosphorus in the phosphate form and total phosphorus, with a total phosphorus concentration of 10 ± 2mg/l and 13 ± 3 mg/l for two wastewater treatment plants in Spain (Vilanova del Valles and La Llagosta). Jolley et al 1998 report 86% of the total phosphorus (4.9 ± 0.2mg/l) of a sewage sample consisting of dissolved ortho-phosphate (4.2 ± 0.2mg/l), with polyphosphate undetected. Patel et al (2006) report 4.8 ± 0.94 mg/l Total phosphorus, consisting of 3.4 ± 0.72 orthophosphate. The average American per person load can be broken down into 1.23g/person/day organic phosphorus as P, 2.05 g/person/day inorganic phosphorus as P. Expressed as Total P, this adds up tp 3.28 g/person/day (Metcalf & Eddy, 2003).

The relatively high temperatures of washing machines and dishwashers, suspended solids, microbiological activity and presence of cations such as calcium in the sewage cause the polyphosphates to be completely hydrolyzed by the time the wastewater reached the treatment plant. Jolley (1993) was unable to detect triphosphates in raw influents to a wastewater treatment plant in Australia. Biological degradation is though the most significant factor in this hydrolysis. Halliwell et al (2000) demonstrated sterilized samples showed little degradation of triphosphate compared to rapid degradation in un-sterilized samples. The chemical half-life of tripolyphosphate in distilled water is up to 5,000 days, however phosphatizing bacteria in natural lakes and rivers accelerate this by up to 1,000 times (Schmitz, 1996). The half life of triphosphate in wastewaters with its slightly higher temperatures than natural systems was measured at 7.3 hrs at 15°C, and only 3.0 hrs at 20°C (Halliwell et al 2000).

Halliwell et al (2000) gives triphosphate decomposition as two steps. Initial decomposition to diphosphate and secondly to orthophosphate:

$$H_5P_3O_{10} + H_20 \rightarrow H_3PO_4 + H_4P_2O_7 \qquad \text{Eqn. No.8}$$

Followed by

$$H_4P_2O_7 + H_20 \rightarrow 2\ H_3PO_4 \qquad \text{Eqn. No.9}$$

Jenkins et al (1971) and Jenkins & Hermanowicz (1991) compared the phosphorus composition of sewage in table no.9:

Table 9. Phosphorus forms in wastewaters

Phosphorus compound group	Jenkins 1971 mg/l P	Jenkins & Hermanowicz 1991 mg/l P
Orthophosphates	5	3-4
Condensed polyphosphates	4	2-3
Organic phosphates	<1	1
Total phosphorus	<10	<7

6.3 Phosphorus Removal

In conventional wastewater treatment, phosphorus is removed by converting the soluble phosphorus ions in wastewater into a solid fraction, followed by physical removal of this solid fraction. This fraction can be an insoluble salt precipitate, a microbial mass in an activated sludge, or a plant biomass in constructed wetlands (de-Bashan et al 2004). Phosphorus compounds undergo three main changes in conventional wastewater treatment:

1. Organic compounds are decomposed and their phosphorus content is converted to orthophosphate.
2. The polyphosphates are converted to orthophosphate
3. Inorganic phosphates are utilized in forming flocs (Mainstone et al 2000).

Approximately 15% of the total phosphorus in the influent can be removed by primary sedimentation (Balmer et al (1988), and between 30-40 % during secondary treatment (CEEP, 1999). The treatment process converts the remaining phosphorus into the highly bio-available form orthophosphate which must be removed prior to discharge. The population size of the wastewater treatment plant will have significant determination on the cost of phosphorus removal. DEFRA (2002) estimate the cost ranges from €0.50/kg P removed for PE >80,000 to €100.5/Kg P removed for <2000 PE for an ELV of 1mg/l. Irish estimates range from €2.40/kg P removed for PE>50,000 to €12.12/Kg removed for PE<500. Costs are based on chemical costs, electrical costs, sludge treatment. Total estimated costs for Ireland to comply with the UWWD are €6million/anum (whole life cost) for all WWTPS (ERM, 2007).

Current technologies available for the removal of phosphorus include:

1. Chemical
    - Precipitation
    - Physical/Chemical adsorption
2. Physical
    - Membrane technologies
    - Filtration for particulate phosphorus

3. Biological
    - Enhanced biological phosphorus removal
    - Assimilation in new biomass

6.4 Chemical Precipitation

The principle of chemical phosphorus removal is to change soluble phosphates into insoluble particulate form by producing chemical precipitates of low solubility, which can be removed during solid/liquid separation (Georgantas et al 2007).

When added to water, salts of iron and aluminum dissociate and react to yield hydrolysis products. It is these hydrolysis products that form the coagulant species that remove turbidity and colour during wastewater treatment processes through flocculation/precipitation.

The mechanism described by Georgantas et al (2007) is:

- Adsorption of phosphate ions onto the hydrolysis products formed during the addition of the salt
- Incorporation of the dissolved phosphates to colloids in suspension
- Removal of phosphates by formation of insoluble salts.

Phosphorus removal is achieved by precipitation using chemical salts according to the reaction:

$Me^{3+} + H_nPO_4^{\,n-3} \leftrightarrow MePO_4$ (Aguilar et al 2002) Eqn. 10

Phosphorus is usually removed from wastewaters by chemical precipitation, using products such as Alum $Al_2(SO_4)_3.14H_2O$, ferric iron salts ($FeCl_3.6H_2O$), ferrous iron salts ($FeCl_2$, $FeSO_4.7H_2O$,) or lime ($Ca(OH)_2$) (Donnert et al 1999). However alum is the most widely used (Georgantas et al 2007). It is generally assumed that phosphorus in the form of orthophosphate is removed by precipitation of phosphate with the metal ion, while the total phosphorus component is removed through interaction with and adsorption onto the flocculated particles (Aguilar et al 2002).

The cost of the chemicals used in the treatment is an important consideration, with costs varying for a tonne of ferrous sulphate at €36 (£32.50) to €111/tonne lime (£100) (Mainstone et al 2000). Balmer et al (1988) however estimate that chemical costs are only about 5% of total costs of capital and operating costs.

A summary of the chemical reactions from (Metcalf & Eddy, 2003) can be given as:

- Lime

  $10Ca^{2+} + 6PO_4^{3-} + 2OH^- \leftrightarrow Ca_{10}(PO_4)_6(OH)_2$ Eqn. 11

- Alum

  $Al^{3-} + PO_4^{3-} \leftrightarrow AlPO_4$ Eqn. 12

- Iron

  $Fe^{3+} + PO_4^{3-} \leftrightarrow FePO_4$ Eqn. 13

The removal of phosphates through chemical precipitation is affected by a number of factors including pH, organic matter and the presence of other metals. Theoretically the minimum solubility of $AlPO_4$ occurs at 6.3, and that of $FePO_4$ at 5.3, however good phosphorus removal occurs anywhere from pH 6.5-7.0. Georgantas (2007) reports maximum removal at pH 5-6. The use of lime is decreasing due to the increase in the amount of sludge produced, as well as the handling and storage requirements associated with lime (Metcalf & Eddy, 2003). However lime sludges do not require stabilization, which may make them attractive for smaller plants (Balmer et al 1988).

6.4.1 Application of chemical precipitants

The salt can be applied at a number of treatment stages;

- Prior to primary sedimentation known as pre-precipitation
- At the biological stage or simultaneous precipitation
- Prior to the secondary clarification stage or post precipitation.

As well as removing phosphorus, pre-precipitation has the advantage of removing significant BOD and suspended solids, reducing the loading on secondary treatment stages, however the sludge may be more difficult to dewater and an additional polymer may be required (Metcalf & Eddy, 2003).

Simultaneous precipitation has the lowest costs, requires less chemicals than primary dosing, produces a more stable sludge but requires greater control of dosing as an overdose of the metal salt may be toxic to the bacteria, and also lower the pH. According to Balmer et al (1988) effluent levels of 1mg P/l are possible.

Post precipitation is not widely used because of its high costs (Morse et al 1993), and increased metal leakage although effluent concentrations of 0.1 mg/l P are theoretically possible, however due to costs, 0.2 mg/l is more likely achieved, though Balmer et al (1988) suggest 0.4 mg/l more likely.

As additional sludge is produced, usually at a rate of 5-7 kg sludge per kg P removed (CEEP 1999), dewatering/wasting, storage and handling implications are associated with such excess sludge. Sludge is potentially unstable under aerobic conditions, and the phosphorus might be released into solution with subsequent storage and handling difficulties (Morse et al 1993).

The average phosphate concentration in raw domestic sewage is 2g/person/day. Typically a dosing rate of 2kg of Ferric solution is required per kg of phosphate removed. Neal et al

(2008), estimate the costs of removal of orthophosphate at €67 (£60) per kg-P for a <10,000 PE WWTP to comply with current consent levels.

Of the chemical dosing processes, calcium dosing to produce calcium phosphate is probably the best environmental option, since the resulting sludge is of agricultural value (Mainstone et al2002).

Other chemical absorbents used with varying degrees of success are red mud, (a waste material from alumina production) (Akay et al 1998) and bauxite (Altundogan et al2001). > 99.8% removal using fly ash (a residue from combustion of coal in power plants) has been reported by Ugurlu et al (1998), Oğuz et al (2003), report 99% removal of phosphorus from a wastewater solution using ‘gas concrete’ a building material made from silica sand, cement, lime water and aluminum cake.

Galarneau et al (1997) reported wastewater treatment plants accepting alum sludges (consisting of predominantly aluminum hydroxide) from water treatment plants can achieve up to 95 % removal of orthophosphate, however removal of organic phosphate was found to be relatively poor.

6.5 Physical Phosphorus removal

Physical processes bring about change in the treatment process through the application of a physical force, and in wastewater treatment include screening, masceration, sedimentation and clarification. Advanced wastewater treatment methods use physical methods such as membrane filtration.

Filtration, defined by Eddy and Metcalf (2003), involves the separation of particulate and colloidal material from a liquid through a porous membrane. The pore size of the membrane being selected for the standard/quality of effluent required, ranging from 0.001-1.0μm.

Filtration can subdivided into

1. Microfiltration with a pore size >50nm can separate oocysts, some bacteria and viruses, suspended solids as well as turbidity.
2. Ultrafiltration, with a pore size 2-50nm can separate macromolecules including proteins, colloidal material and most bacteria.
3. Nanofiltration, with a pore size <2nm can separate smaller molecules, and some hardness.
4. Reverse Osmosis can remove colour, nitrates, hardness and other ions.

The membranes may be made from polypropylene, cellulose acetate, aromatic polyamides and can be a thin sheet or small tube supported on a frame. Hydraulic pressure on the wastewater side of the membrane, or the application of a vacuum on the other side forces the liquid through the pores. Solids are retained on the membrane surface and removed from the effluent (or permeate).

Membrane technologies such as reverse osmosis and membrane bio-reactors are an area of growing interest for wastewater treatment and phosphorus removal. Membranes can remove the particulate phosphorus as well as dissolved phosphorus. Reardon (2006) has suggested current technology allows realistic limits for total phosphorus of 0.04mg/l for membrane filtration and 0.008 mg/l for reverse osmosis.

6.6 Biological Phosphorus Removal

6.6.1 Assimilation

Long used as a method of phosphorus removal, assimilation of phosphorus by plants and using it to form new plant biomass. Landspreading wastewater, assimilation in willow plantations, treatment ponds and constructed wetlands have also traditionally been used.

6.6.2 Constructed/Engineered Wetlands

De-Bashan & Bashan (2004) have described wetlands as basically a container, as small as a bucket or as big as a very large pond, planted with mainly aquatic plants. Emergent or submerged macrophytes work as a biological filter removing organic matter and nutrients, assimilating contaminants directly into their tissues (Maine et al 2007). Microbes in the plant roots are meanwhile degrading other pollutants which the plant can absorb. Constructed wetlands are a relatively low cost, energy efficient, low maintenance (Cameron et al 2003) method of polishing treated wastewater prior to discharge to the aquatic environment. Wetlands are thought to only begin to remove phosphorus after the biochemical oxygen demand has been reduced. Also, as it is a relatively new technology, the long term ability of such wetlands to remove phosphorus has not been proven (Farmer, 1999).

Phosphate removal in constructed wetlands has been described by Lantzke et al (1998) as three parallel removal paths:

1. gravel sorption,
2. microflora processing,
3. macrophyte uptake with gravel sorption.

The removal efficiencies of wetlands vary from 20% P removal (Fisher, 1998) to 98-100% removal (Mann, 1997). Evidently the substrate type (Prochaska et al 2006) and construction plays a major role in the removal efficiency. According to Farmer (1999), for good phosphorus removal, 20-30m^2 is required per person, and even then will not meet the standard set by the urban wastewater directive.

6.7 Enhanced Biological Phosphorus Removal

Biological phosphorus removal (or Enhanced Biological Phosphorus Removal EBPR) from domestic wastewater is dependent mainly on the ability of phosphate accumulating organisms to release phosphate under anaerobic conditions and absorb it under aerobic conditions.

Initially *Acinetobacter* spp. were thought to be the principle organism responsible, but recent studies has shown otherwise (Mino et al 1998). It is now believed the organisms responsible for the EBPR process consist of several different bacterial groups: *Acinetobacter*, *Microlunaatus phosphovorus*, *Lampropedia* spp.

6.7.1 EBPR Process

Under anaerobic conditions, some biodegradable organic matter becomes fermented to short chain fatty acids (SCFAs). These are stored in the cell as poly-hydroxyl butyrates (PHB). This process is fueled by the energy released by the hydrolysis of stored poly-phosphates.

Under aerobic conditions the stored PHB is oxidized and energy in the form of ATP (Adenosine triphosphate) is released allowing the assimilation of soluble ortho-phosphate. The orthophosphates are metabolized by the cell and excess quantities are stored in the cell as polyphosphate. Common heterotrophic bacteria in activated sludge typically have about 1.5-2.0% phosphorus. 20-30% by dry weight stored in volutin granules within the cell can be found in phosphate accumulating organisms (PAOs) (Metcalf & Eddy, 2003).

This storage of excess phosphate formerly known as luxury uptake (Levin and Shapiro, 1965) of phosphorus, has been identified as energy storage by Strom (year unknown). It is this particular ability of the species that is exploited in the nutrient removal process.

Because of the bacterial growth, more PO_4^{3-} is required for poly-P formation than was gained by poly-P-hydrolysis resulting in decrease of PO_4^{3-} in the effluent (Romanski et al 1997). When the cell is cycled between anaerobic and aerobic zones in an activated sludge plant, phosphorus will alternately be released and taken up.

The ability of PAO organisms such as *Acinetobacter*, *Microlunaatus phosphovorus*, *Lampropedia* spp. (Mino et al 1998) to assimilate organic matter in the anaerobic zone gives it a competitive advantage over non-facultative heterotrophic bacteria. Wastage of a fraction of the sludge with its phosphorus rich population can result in removal of large amounts of phosphate (Van Rijn et al (2006). Sludge volumes are not increased, but merely enriched with phosphorus (Mainstone et al 2002). 3.4 kg of sludge is produced per kg phosphorus removed (CEEP 1999).

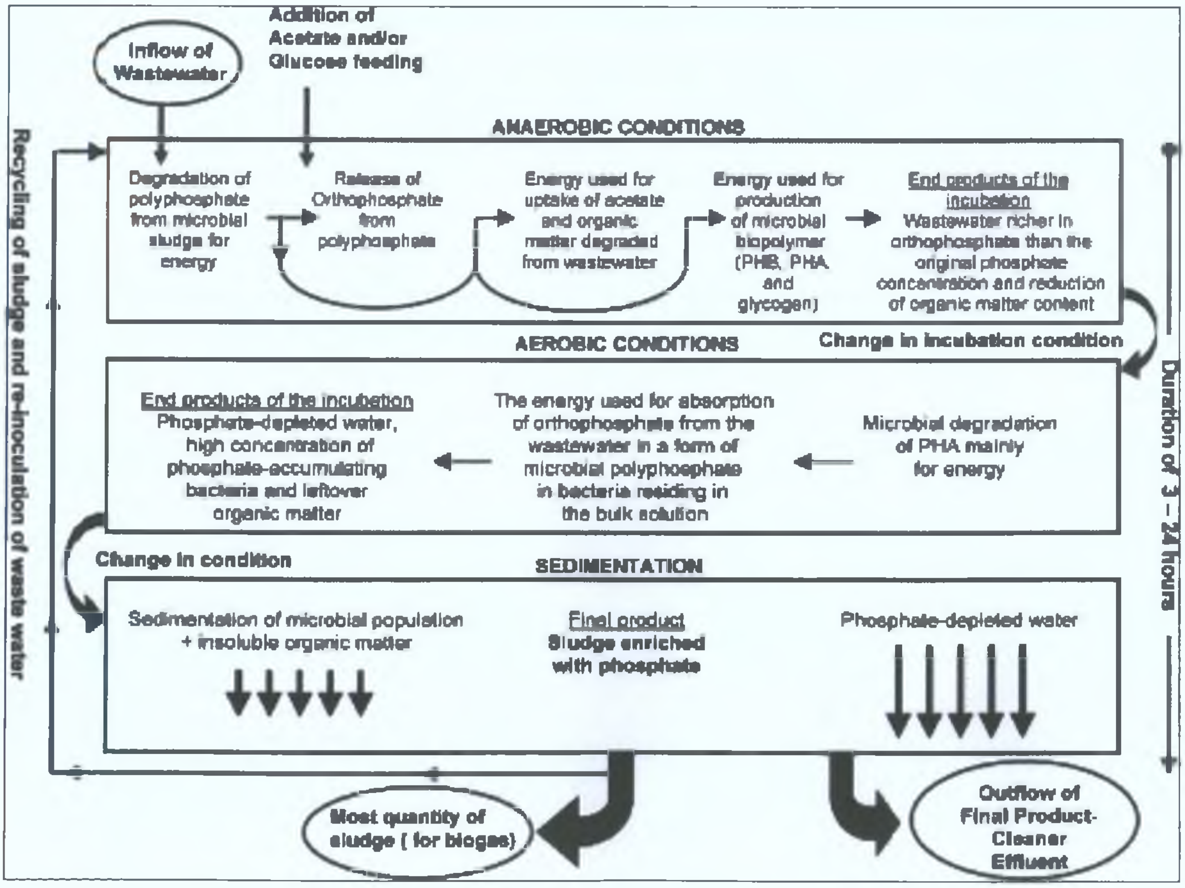


Figure 15. Enhanced Bioloical Phosphorus Removal (de-Bashan, 2004)

6.7.2 EBPR usage

Due to relatively lower capital and operating costs, the use of EBPR is increasing, although according to Lie (1997) often the process kinetics is little understood and the expected results do not appear (Romanski et al 1997) and (Mino et al 2000). According to Mainstone et al (2002) EPBR cannot achieve the same phosphorus removal efficiencies as chemical treatment. Due to variability in the influent load, the nature and variability of the removal process itself, EBPR should be supplemented by simultaneous chemical dosing (Morse et al 1993).

To optimize EPBR, oxygen and nitrate must be excluded from the anaerobic zone. Sufficient SCFA must be present to ensure sufficient PHBs will be biologically stored for use in the aerobic zone. Wastewater is frequently low in SCFAs, and usually a food supplement such as acetic acid is added to the influent. Li et al (2003) report acetic acid exhibited the largest phosphorus release and uptake rates. The final settlement tank must have sufficient dissolved oxygen to remain aerobic.

A BOD:P ratio of 25:1 is considered optimum for biological phosphorus removal. Recycled loads from dewatering operations with very high levels of soluble phosphorus can reduce this ratio, affecting the EBPR process. Such streams should be equalized rather than batched (MPCA, 2006). An added advantage of EBPR, is that PAOs form very dense, good settling flocs, an attribute that has led to the process being used to improve sludge settleability even though phosphorus removal is not required (Metcalf & Eddy, 2003).

7 Monitoring Phosphorus

Chapter Overview

Chapter 7 discusses the forms of phosphorus encountered in environmental phosphorus monitoring, the analytical techniques used to identify the various forms, and how confusion can arise over the myriad forms of phosphorus discussed in the literature and trade.

7.1 Introduction to phosphorus monitoring

The types of chemical species of phosphorus are highly variable within natural waters, but most monitoring programmes rely on defined phosphorus fractions which are sensitive to the storage conditions following sampling (Jarvie et al 2002).

Sorption, hydrolysis, precipitation, complexation and microbiological assimilation and release of phosphorus in the container following sampling mean relative concentrations of the phosphorus fractions may not be representative of those within the river at the time of sampling (Maher and Woo, 1998).

Separation of dissolved and particulate phosphorus is achieved using a 0.45μm filter. The use of the 0.45μm, does not claim a true separation of the dissolved and suspended species of phosphorus, but it does allow for convenient and replicable gross separation (Standard Methods for the Examination of Water and Wastewater, 2005), and represents the soluble, mobile and therefore biologically available form of phosphorus (Haygarth et al 1997)

Following filtration, or not, phosphorus can be determined as several types, based on reactivity. Phosphorus forms that react colourimetrically without a pretreatment such as hydrolysis or digestion of the sample are termed “reactive phosphorus”. Reactive phosphorus although largely a measure of the orthophosphate present, some of the condensed phosphates present (as in detergent STPP) are also unavoidably hydrolyzed.

Phosphorus analyses have one thing in common, they all depend on the inorganic phosphorus species that react colourimetrically, and combine two steps (Standard Methods for the Examination of Water and Wastewater, 2005):

1. Conversion of the phosphorus forms of interest to orthophosphate
2. Colorimetric determination of the dissolved phosphorus.

Inorganic or soluble reactive phosphorus is usually called ortho-phosphate. It is thought that the soluble orthophosphate fraction is the only form directly available, and most easily assimilated by algae and bacteria (Mainstone et al 2002), (Katsaounnos et al 2003). However, Hanrahan et al (2005) suggest other forms of phosphorus other than orthophosphate such as phosphite and hypophosphite are alternative source of bio-available phosphorus for plants.

More complex inorganic phosphate compounds are referred to as "condensed phosphates" or "polyphosphates." The method-based term for these forms is "acid hydrolyzable." Phosphate forms that are converted to orthophosphate by the oxidation of organic phosphate present are known as “organically bound phosphorus.”

The total orthophosphate test measures the orthophosphate that is already present in the sample. The others measure that which is already present and that which is formed when the other forms of phosphorus are converted to orthophosphate by digestion.

7.2 Phosphorus Species

The phosphorus species encountered in environmental monitoring are:

Soluble Reactive Phosphorus (SRP) or Orthophosphate

A measure of the inorganic phosphorus in solution. SRP is also called ‘Dissolved Reactive Phosphorus (DRP)’, ‘Dissolved Inorganic Phosphorus (DIP)’, ‘Filterable Reactive Phosphorus (FRP)’ and ‘Reactive Phosphorus for a filtered sample to a defined filter size eg. RP (< 0.45μm)’ (Jarvie et al 2002). Mainstone et al (2000) call orthophosphate a “theoretical parameter” which cannot be measured analytically.

Molybdate Reactive Phosphorus (MRP)

Molybdate reactive phosphorus gets its name from the test used to determine the inorganic phosphorus species present in a sample. MRP can be either:

- Filtered, thus filtered MRP = SRP or
- Unfiltered, where the MRP = SRP + some of the PP which reacts with the phosphomolybdenum blue reagents.

Total Dissolved Phosphorus (TDP).

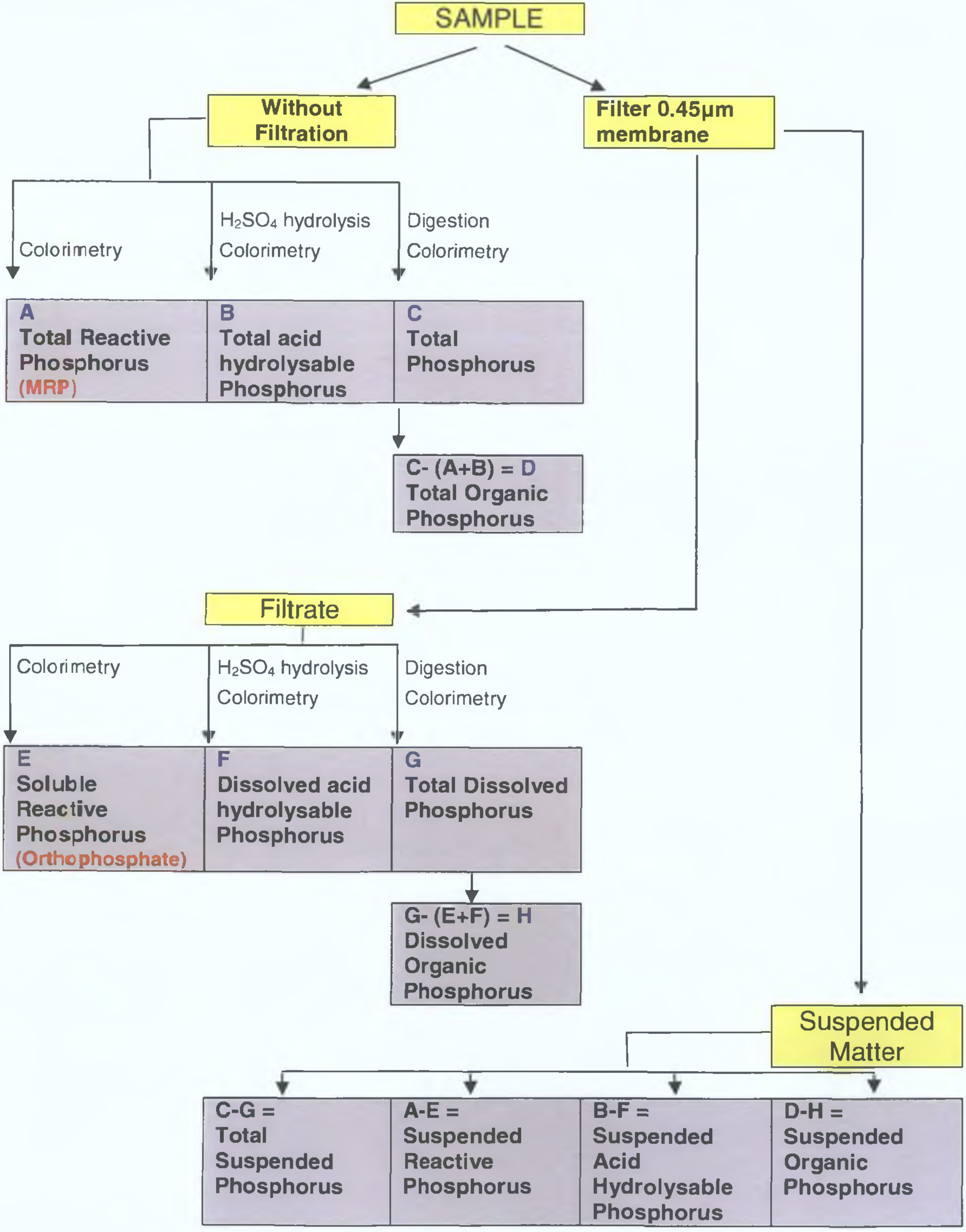
Also called ‘Total Filterable Phosphorus (TFP)’ it is the sum of dissolved inorganic (SRP) and dissolved hydrolysable phosphorus (DHP). DHP is the difference between TPP and SRP.

Total Phosphorus (TP)

Total dissolved phosphorus plus particulate phosphorus. Total phosphorus is the most complete determination of elemental phosphorus regardless of the forms present in the sample. All the forms are converted (via digestion) to orthophosphate which is then determined (EPA, 2001). Particulate phosphorus (PP) is the difference between TP and TDP.

By determining a combination of 2 physical (total and filterable) and 3 chemical (orthophosphate, inorganic and total) it is possible to report 12 fractions:

Table 10. Phosphorus Fractions



7.2.2 Confusion?

As can be seen, the terminology becomes rapidly confusing to the uninitiated. Jarvie et al (2002) calls the current system "confusing and inexact". Mainstone et al (2000) discussing phosphate monitoring, admonishes the UK Environment Agency, for using misleading and confusing terminology, using soluble reactive phosphorus (SRP), when it was unfiltered MRP that was measured, and recommends that correct terminology be used, while in some literature the terminology is so vague, it is unclear what was actually determined (Mainstone et al year unknown).

Haygarth attempted to bring clarity to the subject in 2000, by defining "Reactive" phosphorus as that which readily reacts with the ammonium molybdate method of Murphy and Riley. That which doesn't but requires digestion, was defined as "unreactive P". Total Phosphorus therefore is the total of "reactive P" and "unreactive P". According to Haygarth (2000), any attempt to classify phosphate as orthophosphate, organic or inorganic in context with the Murphy and Riley method will be technically incorrect as the Murphy and Riley Method may overestimate the phosphorus due to loosely bound inorganic and organic forms reacting with the reagents. Any classification of nomenclature using "dissolved", "soluble", or "particulate", is also potentially flawed due to the subjectivity of membrane size used by the analyst, and colloidal phosphorus reacting (Haygarth, 2000) and (Baldwin, 1998). Unless the definition includes how the phosphorus was measured, the result is open to misinterpretation and inappropriate recommendations (Pierzynski, 2000).

The decision of the filter size used is an arbitrary choice by the analyst, as no separation is truly complete (Methods for the Examination of Waters and Associate Materials, 1980). Some analysts filter in the field, and some filter in the laboratory and as container adsorption is significant, it is clearly an area in need of greater agreement regarding terminology and analysis. The 0.45µm membrane used is merely a convenient technique that allows for repeatability. The literature differs in whether or not immediate or later laboratory filtration causes a significant difference in the amount of soluble reactive phosphorus that will be determined. Lambert et al (1992) claim it must be within an hour of sampling, or otherwise the results will be meaningless, while others demonstrated very little changes occur over a few hours, but are subject to changes over days. As a precaution, it is recommended that samples are filtered in the field (Bull et al 1994: Haygarth et al 1995).

According to the EPA, caution should be exercised when reviewing any phosphorus analytical work, due to it existing in bound and unbound forms, which are often difficult to separate fully, and that orthophosphate is “broadly equivalent” to Molybdate-Reactive Phosphate (EPA, 2001), However in 1997 the EPA stated that MRP is ‘unfiltered’.

Baldwin (1998) suggests the molybdenum method may be *overestimating* the amount of ortho-phosphate present, possibly due to some organic phosphorus being hydrolysed during analysis. Haygarth et al (1997) and Stainton (1980) agree, reporting that the molybdate reaction also causes loosely bound inorganic and organic forms to react. Tarapchak (1983) found that the molybdenum enhances bound orthophosphate release, and produces sensitive complexes with dissolved organic forms. Jones (1982) determined that the free orthophosphate only represented a fraction of the total MRP. Haygarth et al (1997) determined that the MRP was 50% greater in <0.45μm filtered natural samples than in ultra filtered (<1000 Molecular weight) samples. Similar work by Baldwin (1998) found that the free orthophosphate ion accounted for only 20% of the reactive phosphate in water samples. Such work demonstrates that MRP is not synonymous with being a free and soluble form of phosphorus.

CEEP (1999) suggest it would be advantageous to set environmental quality targets based on total phosphorus rather than orthophosphate, as this will allow easier linking of point and non point sources, and provide clarity. The Irish phosphorus regulations require MRP to be measured, while the Urban Wastewater directive requires TP to be measured in effluents and the receiving waters. CEEP (1999) report greater correlation between chlorophyll-a and TP than with SRP.

The Environment Agency in the UK is proposing to introduce Environmental Burden (EB) methodologies into its regulatory activities. An Environmental Burden is defined as “a quantitative measure of the potential contribution of released substances to a particular environmental impact.” EA (2003). It is hoped these EBs will convey information about industrial discharges more usefully, as well as improving efficiencies and effectiveness’s in their activities. The EB for phosphorus is to be expressed as “Phosphorus, Total, tonnes as P”. No allowance is to be made for the phosphorus species usually present in wastewater discharges, but that the dissolved phosphorus equals total phosphorus. This gives a “worst case” scenario of the potential impact of discharges.

7.2.3 Phosphorus to phosphate conversions

Phosphorus has an atomic weight of 30.97g
Oxygen has an atomic weight of 15.999g
$\therefore$ PO_4 has an atomic weight of 94.97g
& P_2O_5 has an atomic weight of 141.94g

1 mg as PO_4 = 30.97/94.97 = 0.33 mg as P

Or

1mg as P = 3.07 mg as PO_4

Thus to convert mg P to mg PO_4, multiply by 3.07.

To convert mg PO_4 to mg P, divide by 3.07.

To convert mg/l P to mg/l P_2O_5 multiply by 2.3

To convert mg/l P_2O_5 to mg/l P divide by 2.3,

7.3 Laboratory Analysis

Most workers (Maine et al (2007), Jarvie et al (2006), Bowes et al (2005), Kurz et al (2005), Smith et al (2001), Neal et al (2000), are using the 1962 Murphy and Riley molybdenum blue for orthophosphate. Based on a method by Murphy and Riley (1962), the basic premise of the phosphate and molybdate method is formation of heteropoly phosphate-molybdate acid which on reduction with ascorbic acid produces a blue colour, the intensity of which is proportional to the orthophosphate concentration.

Sjösten et al (1997) claim the formation rate of the analyte is an “insidious” source of error, resulting in an underestimation of the true concentration, while the degree of agitation and mixing of a sample will affect results due to a time dependent desorption reaction of orthophosphate from suspended matter (Standard Methods for the Examination of Water and Wastewater, 2005).

Silica along with pH and temperature of reaction are significant interferences for the determination of phosphorus species in waters although the effect of silica decreases as the waters become more polluted (Neal et al 2000).

Other workers in the field such as Gerogantas et al (2007) measured orthophosphate using the vanadate-molybdate method using a Camspec M302 spectrophotometer at 470nm, and Karageorgiou et al (2007) used an ICP-AES technique as did Smith et al (2001) for total phosphorus. Patel et al (2006) used a HACH for total phosphorus, and measured soluble phosphate on a Walter IC-Pak column. Jolley et al (1998) separated phosphate species by anion exchange chromatography using Dowex 1-X8 resin.

8 Materials and Method

Chapter Overview

This chapter identifies the materials used, and both orthophosphate and the total phosphorus procedures used and the analytical techniques. The materials section includes all materials used from the sample collection, through preservation to the instrumentation and reagents used. A brief explanation of the theory behind the test, as well as how the instrument operates is included.

8.1 Materials

8.1.1 Sampling Materials

Disposable 2L PTFE sample containers with screw top PTFE lid.
Disposable 100mls PTFE preservation containers with screw top PTFE lid.
Analar Grade Suphuric acid
Grade Sodium Hydroxide
Flow proportional composite samplers with refrigerated HDPE sample containers.

8.1.2 Analytical Materials

1. Heating Block with safety shield set at 150 °C +/- 3 °C
2. HACH DR2000 Spectrophotometer (Total Phosphorus)
3. Prepared Total Phosphorus Test 'N Tube Reagent set
   (This includes: PhosVer 3 Phosphate Powder Pillows, Potassium Persulphate Reagent Powder Pillows, Total and Acid Hydrolyzide Test Vials, and 1.54 N Sodium Hydroxide Standard Solution)
4. Konelab 20 Analyser (Orthophosphate)
5. Multicell Curvettes

6. Test Tube rack
7. Nitric Acid washed and rinsed Pipettes, 2, 5, and 10 ml
8. Calibrated Timer
9. 0.45μm filters and syringe.

8.1.3 Analytical Reagents Used

1. Standard KH_2PO_4 Solution (50 mg/l) and Quality Control Standard $K_4O_7P_2$ (100 mg/l)
2. Antimony potassium tartrate solution
3. Ammonium molybdate
4. Dilute sulphuric acid solution (5N H_2SO_4)
5. Ascorbic acid solution
6. Standard and QC stock K_2PO_4 solutions (1000 mg o-PO_4^{3-} /l P)
7. Working solutions: Reagent 1 and Reagent 2.

8.2 Total Phosphorus and Molybdate Reactive Phosphorus: Methods and Procedures

8.2.1 Total Phosphorus Method

(Reference: Chemical Procedure No. 20 – Cork County Council Wastewater Laboratory, 2009)

Scope of Method

Working Range: (0.2 to 2.50 mg/l TPO_4-P)

Method Detection Limit 0.20mg/l TPO_4-P

Undiluted samples less than 0.20mg/l are reported as < 0.2mg/l TPO_4 -P

Principle of Method

Phosphates present in organic and condensed inorganic forms (meta-, pyro- or other polyphosphates) must be converted to reactive orthophosphate before analysis. Pre-treatment of the sample with acid and heat provides the conditions for hydrolysis of the condensed inorganic forms. Organic phosphates are converted to orthophosphates by heating with acid and persulphate. Orthophosphate reacts with molybdate in an acid medium to produce a phosphomolybdate complex. Ascorbic acid then reduces the complex, giving an intense molybdenum blue colour.

Storage and Preservation

Samples are adjusted to a pH of 2 or less with 0.2 ml of concentrated Sulphuric Acid and refrigerated at ≤ 4 °C but > 0 °C. Samples should be analyzed within 28 days of preservation.

Note: The samples are neutralized with sodium hydroxide and warmed to room temperature before analysis. As samples are neutralized a bias has been introduced. The volume change, while still less than 1%, will contribute to marginally lower results by <1%.

Interferences

Large quantities of sample turbidity may cause inconsistent results in the test because the acid present in the powder pillows may dissolve some of the suspended particles and because of variable desorption of orthophosphate from the particles.

The PhosVer 3 Phosphate Reagent Powder Pillows should be stored in a cool dry environment.

The following may interfere when present in concentrations exceeding these listed below:

Substance	Interference Level (mg/l)
Aluminium	200
Chromium	100
Copper	10
Iron	100
Nickel	300
Silica	50
Silicate	10
Zinc	80

Arsenate and hydrogen sulphide interfere at any level.

Highly buffered samples or extreme sample pH may exceed the buffering capacities of the reagents and require sample pre-treatment.

8.2.2 Total Phosphorus Procedure

Stage 1

(a) Turn on the Heating block and heat to 150°C.

Note: Ensure Heating block is placed in fume hood with plastic shield surrounding it.

(b) Neutralize preserved samples with 10N NaOH by adding drop wise and checking with pH paper. Allow samples to reach room temperature before analysis.

(c) Using a 5ml disposable pipette transfer 5ml of sample to a Total and Acid Hydrolyzable test vial.

(d) Add contents of one potassium persulphate powder pillow for phosphonate to the vial.

(e) Cap tightly and shake to dissolve.

(f) Heat the vial for 30 minutes at 150°C in the heating block.

Note: remove plastic shield when digesting samples in the fume hood.

(g) Carefully remove the vials from the Heating block. Place them in a test tube rack and allow to cool to room temperature.

Stage 2

(h) Using a 2ml disposable pipette add 2.0mls of 1.54N sodium hydroxide to each vial.

(i) Add the contents of one PhosVer 3 phosphonate reagent powder pillow to each of the vials.

(j) Cap tightly and shake for 10-15 seconds.

Note: the powder will not completely dissolve.

(k) Set a timer to allow a 2-minute waiting period.

Stage 3 – Operation of DR2000 Spectrophotometer

(l) Turn on the Dr2000 instrument. Enter the user-stored programme for reactive phosphorus Test n' Tube. Press **Enter**. The display will show **Dial to 890**.

(m) Rotate the wavelength dial until the small display shows 890nm. When the correct wavelength is dialed in, the display will quickly show **ZERO SAMPLE.**

(n) Place the vial adaptor into the cell holder with the marker to the right.

(o) Clean the outside of the vial with a paper towel.

(p) Place the blank in the adaptor with the Hach logo facing to the front of the instrument. Place the cover on the adaptor.

(q) Press **ZERO**. The display will show **ZEROING** and then **TP**.

(r) Repeat steps (o) and (p) for the rest of the batch. Press **READ**. The display will show **READING** and then the results in **mg/l TP** will be displayed.

8.2.3 References

1. HACH Water Analysis Handbook 1997 Page 1040.
2. Standard Methods for the Examination of Water and Wastewater, 21st Edition 2005, A.P.H.A., A.W.W.A., W.E.F., Section 1060B, Table 1060I, Pages 1-33, 1-34.
3. HACH Water Analysis Handbook 1997 Page 1046, 1047.
4. HACH Water Analysis Handbook 1997 Page 1041.
5. Standard Methods for the Examination of Water and Wastewater, 21st Edition 2005, A.P.H.A., A.W.W.A., W.E.F., Section 4500-P.E.3f, Page 4-154.
6. HACH Water Analysis Handbook 1997 Page 1042 - 1045.
7. HACH DR2000 Spectrophotometer Handbook Page 1 - 22

8.3.1 Molybdate Reactive Phosphate Method

(Reference: Chemical Procedure No. 22 – Cork County Council Wastewater Laboratory, 2009)

Scope of Method

Working Range = 0.05 to 1.00 mg o-PO_4^{3-} -P/l

Method Detection Limit = 0.02 mg o-PO_4^{3-} -P/l.

Principle of measurement

The phosphate ion (o-PO_4^{3-}) reacts with ammonium molybdate and antimony potassium tartrate (catalyst) under acidic conditions to form a 12-molybdophosphoric acid complex. This complex is reduced with ascorbic acid to form a blue heteropoly compound which absorbs light at 880nm. The absorbance is proportional to the concentration of the phosphate ion (o-PO_4^{3-}).

Sampling and storage

Samples containing low concentrations of phosphorus should not be stored in plastic bottles unless in a frozen state as phosphorus may be adsorbed onto the walls of plastic bottles. Never use commercial detergents containing phosphate for cleaning glassware in phosphate analysis. Rinse all glass containers with hot dilute HCl and rinse in distilled water. Refrigerate at ≤ 4 °C but > 0 °C for samples to be analysed within 48 hours. Freeze samples if analysis is delayed for a maximum period of 14 days.

Interference

Arsenates (as low as 0.1 mg As/l) react with the molybdate reagent to produce a blue colour similar to that formed with phosphate.

Hexavalent chromium and Nitrite (NO_2^-) interfere to lower the true value by 3% at concentrations of 1 mg/l and by 10-15% low at 10 mg/l.

Silica forms a pale blue complex which absorbs at 880nm. This interference is insignificant, as to produce a positive 1mg/l error in phosphate would require a silica concentration of approximately 4,000 mg/l.

8.3.2 Molybdate reactive Phosphate Procedure

Sample Analysis.

Ensure the calibration curve is valid (i.e. within date). At the Main screen click 'Calibration results' or press F7. Select the test from the drop down box to ensure that the curve is in date. Prepare a new calibration curve monthly or when new stock is prepared.

Click on the **'Main'** icon. Load the segment with samples. Dilute if necessary to bring sample concentration within the working range. Include a QC sample (Concentration = 0.50 mg/l) with every batch. Insert standards for every 10 samples analysed. The standards are 0.2 mg/l and 0.8mg/l concentration.
Analyze a blank of 100 ml 18 megaohm - Cm water. Check for a high reading.
Click **'Sample'** icon. Click **'Insert segment'.** Insert the segment when prompted. Repeat for other segments if needed.

Click 'Main' icon. Click on the number of the segment inserted on the right of the window. Into each of the blank spaces, enter the sample ID. (If a QC or standard is in a space, type in the QC number and concentration. Don't use the drop down box and select from the list). Press return on the keyboard to move to the next space.

When all the samples have been entered, click **'More'** , click **'Insert requests'** or press F2 to bring up the test request window.

Select the tests that are required for that segment. Press OK. Repeat for all the other segments containing samples to be analyzed for molybdate reactive phosphate.

When all are entered, click **'Main'** and press the green start key on the keyboard. (The most recent calibration curve accepted for the test selected is automatically used).

When analysis is completed, check that the QC and standard samples are within parameters. If the sample result is > 1.00 mg/l, dilute the sample and repeat. Click the name of the tests to be accepted. Click '**Accept Page'** icon.

Remove all segments, reagents and enter standby-by mode.

Reporting of Results

Report results that are less than the lowest calibration standard as <0.05 mg $o\text{-}PO_4^{3}\text{-}P$ /l. Report results to 2 decimal places.

Conversion Factors: 1 $o\text{-}PO_4^{3-}\text{-}P$ = 3.07 $o\text{-}PO_4^{3-}$

References

1. Standard Methods for the Examination of Water and Waste Water, 21st Edition 2005, A.P.H.A., A.W.W.A., W.E.F., Section 4500-P E.1 Page 4-153.
2. Standard Methods for the Examination of Water and Waste Water, 21st Edition 2005, A.P.H.A., A.W.W.A., W.E.F., Section 4500-P A.5, Page 4-149, Section 1060B Page 1-29 to 1-34.
3. Standard Methods for the Examination of Water and Waste Water, 21st Edition 2005, A.P.H.A., A.W.W.A., W.E.F., Section 4500-P E.1.b, Page 4-153.
4. AquaChem 200 Step-by-Step User Guide. Serosep Ltd.
5. Konelab Aqua Reagent Manual Version 2003 Issue 1.
6. Standard Methods for the Examination of Water and Waste Water, 21st Edition 2005, A.P.H.A., A.W.W.A., W.E.F., Section 4500-P E.3 Page 4-154.
7. Konelab Aqua Reference Manual. Thermo Electron Corporation.

9 Results

Chapter Introduction;

A brief overview of each agglomeration is given, including the geographical location, marked with a ○ on the map of each agglomeration, the population equivalent of the agglomeration served by the treatment plant, and a description of the treatment process in each plant. Organic loading to a wastewater works are measured in Population Equivalents. A Population Equivalent is defined by the Urban Wastewater regulations as the organic biodegradable load having a five-day biochemical oxygen demand (BOD5) of 60 g of oxygen per day.

Analytical results are given for each of the wastewater treatment plant's influent and effluent for orthophosphate and total phosphorus. The percentage orthophosphate of the total phosphorus is determined.

Plants >2000PE are required to be monitored for BOD, COD and suspended solids under the terms of the Urban Wastewater Directive, and plants >10,000 PE discharging to sensitive waters, for total phosphorus and/or total nitrogen also. There is a requirement that these effluent samples are 24hour, flow proportional composite samples. Under the Urban Wastewater Directive, there is no requirement to monitor orthophosphate in either the influents or effluents, so little information exists for Irish wastewaters. The receiving waters are however, required to be monitored for orthophosphate.

Where composite samplers are in place on influents, these also were taken, but usually influent samples were grab samples, except for Blarney, Ballincollig, Mallow, Fermoy and Mitchelstown. All influent samples were taken post maceration and prior to any mixing with return activate sludge (RAS). For this reason Macroom and Carrigtohill were not included in the study as it was difficult to regularly take a sample prior to RAS.

Samples were taken by the author and staff from the Council's wastewater Laboratory over the course of the project during scheduled monitoring visits to Council wastewater treatment plants.

9.1 Ballincollig WWTP

Ballincollig is serviced by a partially and fully combined sewer network. Other than recent developments, (mid 90s on), all storm water in the agglomeration discharges to the WWTP leading to severe problems such as solids washout. The treatment plant was constructed in late 1970's replacing an older stone filter treatment plant. The 2006 census determined the population served by the treatment plant as 16,339.

The plant currently has a BOD loading of 1890 Kg/day giving a PE capacity of 32,000 PE. Hydraulic capacity is 15,000 PE at 6DWF. This restriction in capacity is due to be mitigated by the installation of a new clarifier. Current estimated load is 20,200PE, with approximately 12.5% contributed by non domestic discharges. Treatment process consists of a 9000m^3 extended aeration carousel type activated sludge treatment plant with twin settling tanks. There is currently no additional phosphorus removal. The treatment plant discharges to the River Lee.

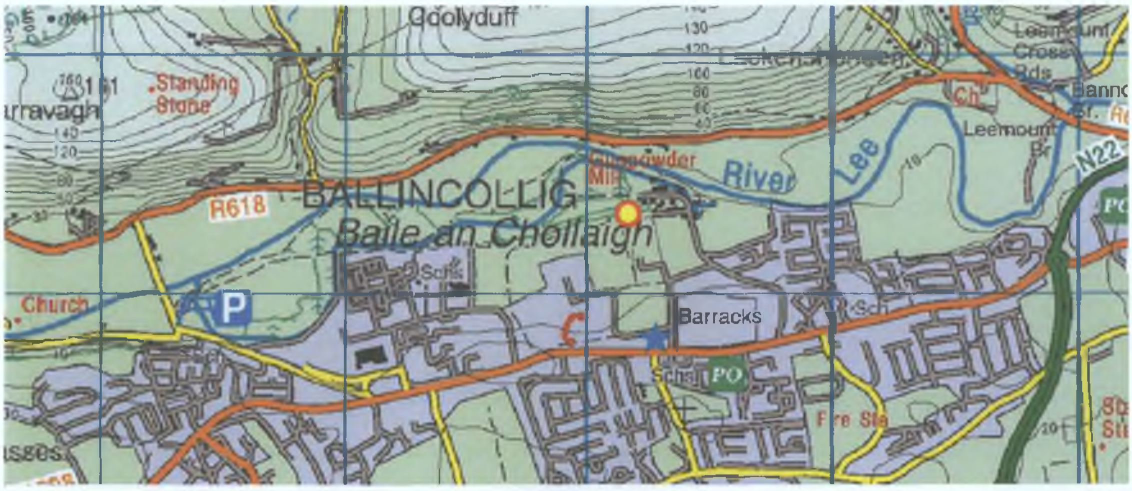


Figure 16. Ballincollig WWTP. Scale1:17509

Ballincollig Results

	Influent			Effluent		
Sample Date	T-P mg/l P	MRP mg/l PO_4-P	% MRP/TP	Total mg/l	MRP mg/l PO_4-P	%
08/08/2007				5.43	5.05	93.0
05/09/2007	12.63	7.71	61.0	8.1	7	86.4
07/02/2008	8.95	5.41	60.4	4.58	4.51	98.5
06/03/2008	14.5	8.78	60.6	6.8	5.85	86.0
03/04/2008	12.08	8.27	68.5	6.6		
05/06/2008	12.85	11.15	86.8			
10/07/2008				6.53	5.46	83.6
22/01/2009	3.85	2.08	54.0			
05/03/2009	11.53	7.24	62.8			
02/04/2009	16.2	9.76	60.2	5.93	4.46	75.2
Average	11.6	7.6	64.3	6.4	4.6	87.1
Min	3.9	2.1	54.0	4.6	4.5	75.2
Max	16.2	11.2	86.8	8.1	7.0	98.5
Std. Dev.	3.8	2.8	9.9	1.1	1.0	8.0

9.2 Bandon WWTP

The original WWTP in Bandon was built in the 1960's and upgraded in 1993 to treat a PE of 20,0000. The majority of the agglomeration is served by a combined sewerage system, treating flows up to 3DWF. The current load is 8178PE. Included in this loading is 80m^3/day leachate from Derryconnel Landfill site.

Treatment consists of primary settlement, secondary treatment via activated sludge operating in parallel with a percolating filter system. Nutrient removal and tertiary treatment are not provided in the treatment plant.

The treatment plant discharges to the Bandon River, designated sensitive waters under the Urban Wastewater Treatment Regulations (S.I. 254/2001). Although recent years have seen an improvement in the receiving waters from Q3 in 1997 to Q4 in 2006, elevated phosphate levels are still recorded downstream.

Figure 17. Bandon WWTP Scale1:17509

Bandon Results

	Influent			Effluent		
Sample Date	**T-P** **mg/l P**	**MRP** **mg/l PO_4-P**	**% MRP/TP**	**Total** **mg/l P**	**MRP** **mg/l PO_4-P**	**%**
09/08/2007				4.33	3.63	83.8
07/02/2008	4.7	2.85	60.6	1.37	1.13	82.5
06/03/2008	3.82	2.98	78.0	3.13	2.54	81.2
03/04/2008	6.43	3.34	51.9			
22/05/2008				4.3	3.03	70.5
04/06/2008	5.15	2.87	55.7	5.05	3.64	72.1
17/07/2008	8.75	5.78	66.1	4.23	3.4	80.4
22/01/2009	3.88	2.44	62.9	3.4		
Average	5.5	3.4	62.5	3.7	2.9	78.4
Min	3.8	2.4	51.9	1.4	1.1	70.5
Max	8.8	5.8	78.0	5.1	3.6	83.8
Std. Dev.	1.9	1.2	9.1	1.2	1.0	5.7

9.3 Blarney WWTP

The wastewater in the twin settlement of Blarney-Tower is collected in a partially combined foul and separated foul network. Blarney WWTP is designed for a population equivalent (PE) of 13, 000 with a BOD loading of 780Kg/day. The maximum hydraulic capacity of the treatment plant is 384m^3/hour (2.7 DWF). The treatment plant has two treatment streams: 50% of flow is treated via an aeration phase and a secondary settlement phase. The other 50% passes into a recently added treatment stream, which includes an anaerobic stream, anoxic and aeration phase, and secondary settlement phase. Phosphorus removal is achieved by Ferric sulphate dosing at the biological stage.

The domestic population of Blarney is now 5,226 (Census, 2006). Other sources of influent that contribute to the loading include commercial premises, schools and tourism. The plant was recently upgraded from 6500 PE to 13,000.

Figure 18. Blarney WWTP
Scale 1:33416

Blarney Results

	Influent			Effluent		
Sample Date	**T-P mg/l P**	**MRP mg/l PO_4-P**	**% MRP/TP**	**Total mg/l P**	**MRP mg/l PO_4-P**	**%**
21/08/2007	7.15	4.48	62.7	2.2	2.05	93.2
06/09/2007	8.78	6.39	72.8	2.22	2.19	98.6
07/02/2008	12.6					
06/03/2008	7.33	4.4	60.0	2.09	1.83	87.6
06/05/2008				1.94	1.79	92.3
04/06/2008	5.18	3.08	59.5	0.56	0.52	92.9
10/07/2008				1.42	1.22	85.9
21/08/2008				0.95	0.87	91.6
22/01/2009	3.88	1.72	44.3	1.3		
05/03/2009	3.78	3.29	87.0			
Average	7.0	3.9	64.4	1.6	1.5	91.7
Min	3.8	1.7	44.3	0.6	0.5	85.9
Max	12.6	6.4	87.0	2.2	2.2	98.6
Std. Dev.	3.1	1.6	14.4	0.6	0.6	4.1

9.4 Castlemartyr WWTP

Wastewater in Castlemartyr is collected in a partially combined drainage network. The plant has a nominal capacity of 2000PE. The treatment works consist of inlet works, 12m diameter x 2.5m height aeration tank with fine bubble aeration, 9m diameter x 1.8m high clarifier. The current residential population is estimated at 1685, with additional loading from schools, commercial premises and tourism. The treatment plant currently discharges to the Kiltha River. There are no phosphorous removing devices at the plant.

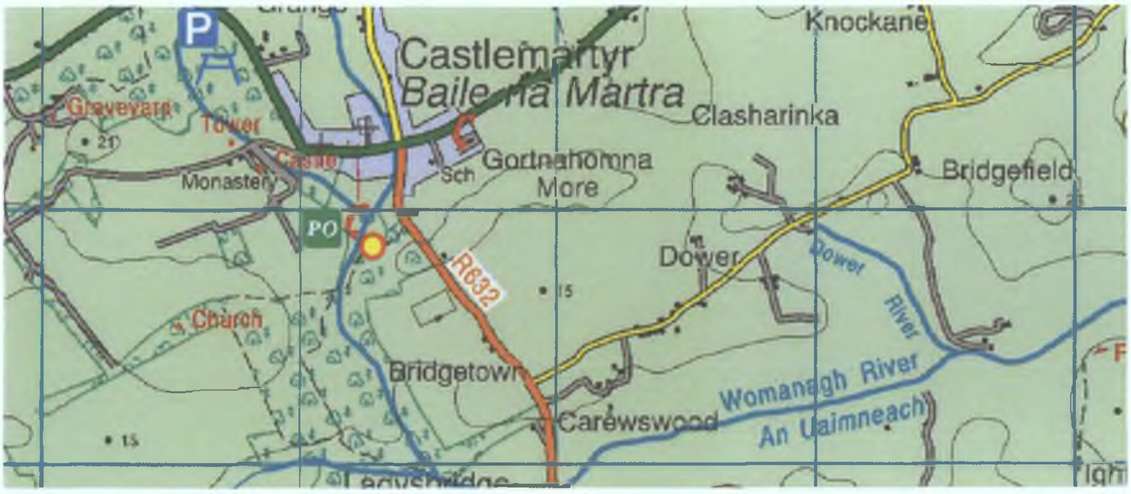


Figure 19. Castlemartyr WWTP
Scale 1:17509

Castlemartyr Results

	Influent			Effluent		
Sample Date	**T-P** mg/l P	**MRP** mg/l PO_4-P	**% MRP/TP**	**Total** mg/l P	**MRP** mg/l PO_4-P	**%**
08/08/2007				1.29	0.4	31.0
05/09/2007	33	12.44	37.7	1.41	1.28	90.8
07/02/2008	5.23	3.23	61.8	2.1		
28/02/2008		4.9		1.99	1.9	95.5
13/03/2008				1.3	0.82	63.1
03/04/2008		4.52		4.75	4.02	84.6
22/05/2008				1.32	1.16	87.9
10/07/2008				0.68	0.27	39.7
17/07/2008	13.8	9.63	69.8	1.19	0.72	60.5
03/09/2008				2.05	1.57	76.6
26/03/2009	4.75	2.2	46.3			
Average	14.2	6.2	53.9	1.8	1.3	70.0
Min	4.8	2.2	37.7	0.7	0.3	31.0
Max	33.0	12.4	69.8	4.8	4.0	95.5
Std. Dev.	13.2	4.0	14.6	1.1	1.1	23.0

9.5 Charleville WWTP

Charleville wastewater treatment plant was originally designed for a PE of 15,000. Design DWF is 2,050 m^3/day, although the plant can cope with up to 6DWF. The 2006 census of Charleville has a population of 2,984, with additional loading from schools, commercial activities and tourism.

The collection system for Charleville is separated foul and storm sewers. Treatment consists of inlet screening and flow controls, 2 No. oxidation ditches, and 2 No. clarifiers. However as the plant is currently operating at less than half capacity, only one oxidation ditch and clarifier is currently in use. Final discharge is to the Charleville stream. There is no phosphorus removal at the plant.

Figure 20. Charleville WWTP.
Scale

Charleville Results

	Influent			Effluent		
Sample Date	**T-P** **mg/l P**	**MRP** **mg/l PO_4-P**	**% MRP/TP**	**Total** **mg/l P**	**MRP** **mg/l PO_4-P**	**%**
13/09/2007	2.38	1.82	76.5	1.75	1.44	82.3
16/01/2008	3.1	2.3	74.2	1.1	0.7	63.6
14/02/2008	3.85	0.96	24.9	1.2	0.86	71.7
08/04/2008	2.4	2	83.3	2	1	50.0
10/04/2008	3.15	1.98	62.9	1.64	1.41	86.0
11/06/2008	2.5	1.3	52.0	1.1	0.8	72.7
17/07/2008	1.57	0.72	45.9	1.38	1.12	81.2
09/10/2008	2	0.1	5.0			
19/12/2008		1.74				
05/03/2009	0.97	0.94	96.9			
02/04/2009	4.28	3.37	78.7			
Average	2.6	1.6	60.0	1.5	1.0	72.5
Min	1.0	0.1	5.0	1.1	0.7	50.0
Max	4.3	3.4	96.9	2.0	1.4	86.0
Std. Dev.	1.0	0.9	28.4	0.4	0.3	12.5

9.6 Clonakilty WWTP

Wastewater in Clonakilty is collected in a partially combined foul and surface water collection system consisting of both gravity and pumped systems. The original design loads for the WWTP are 5,333 PE, with BOD loading of 364kg/day and hydraulic load 102 l/s (DWF). The treatment plant was constructed in 1987 and is currently overloaded. Although the 2002 Census gives the population of Clonakilty at 2930, the loading on the plant rises to 15,000 PE during summer months.

The treatment works consist of grit removal and classifier, screening, 2 no. racetrack type oxidation ditches and 2 no. settling tanks. An upgrade of the plant to a 20,500 PE has been approved under the Water Services Investment Programme, which will involve the installation of an additional oxidation tank and clarifier and primary sedimentation tanks. The pollution load from the Clonakilty agglomeration arises from local population, Shannonvale Chickens, Clona Milk Dairies, Irish Yoghurts, hospitals, schools and hotels. Local industries make up 33% of the loading to the treatment plant. Treated effluent discharges into the tidal reach of the River Feagle adjacent to the plant. There are phosphorus removal measures.

Figure 21. Clonakilty WWTP
Scale1:17509

Clonakilty Results

	Influent			Effluent		
Sample Date	**T-P** mg/l P	**MRP** mg/l PO_4-P	**% MRP/TP**	**Total** mg/l P	**MRP** mg/l PO_4-P	**%**
09/08/2007				1.46	1.18	80.8
07/02/2008	3.15	1.02	32.4	2.2	1.58	71.8
06/03/2008	5.2			2.85	1.95	68.4
03/04/2008				2.33	1.53	65.7
22/05/2008				2.15	1.63	75.8
11/06/2008				7.78	7.63	98.1
19/06/2008		3.59		4.39	3.98	90.7
03/09/2008				1.78	0.6	33.7
18/12/2008		2.92				
22/01/2009	3.23	1.76	54.5			
12/03/2009		3.46				
Average	3.9	2.6	43.5	3.1	2.5	73.1
Min	3.2	1.0	32.4	1.5	0.6	33.7
Max	5.2	3.6	54.5	7.8	7.6	98.1
Std. Dev.	1.2	1.1	15.6	2.1	2.3	19.4

9.7 Dunmanway WWTP

The wastewater treatment plant in Dunmanway had an original design capacity of 1000PE. Constructed in the 1960's it has seen no significant upgrade since then. The current load to the treatment plant of 5400 PE is in well excess of design load.

The treatment works consist of 2 No. Imhoff tanks for primary settlement, 2 No. percolating filters for secondary treatment and final humus tanks prior to discharge to the River Bandon. The current plant is due to be replaced completely rather than upgrading, with a new design capacity of 3500 PE.

Figure 22. Dunmanway WWTP
Scale 1:17509

Dunmanway Results

	Influent			Effluent		
Sample Date	T-P mg/l P	MRP mg/l PO_4-P	% MRP/TP	Total mg/l P	MRP mg/l PO_4-P	%
09/08/2007				3.48	2.54	73.0
06/09/2007				7.55	5.85	77.5
07/02/2008	2.9	1.65	56.9	2.28	1.48	64.9
03/04/2008		3.71		4.28	2.08	48.6
22/05/2008				1.4	0.96	68.6
04/06/2008	2.21	0.9	40.7	1.83	1.09	59.6
19/06/2008		6.67		3.53	2.26	64.0
02/07/2008	2.12		0.0	1.82	0.5	27.5
30/07/2008	2.33	1.83	78.5	2.44	1.48	60.7
10/09/2008				2.49	1.99	79.9
06/02/2009	1.93	1.85	95.9			
12/03/2009		3.04				
Average	2.3	2.8	68.0	3.1	2.0	62.4
Min	1.9	0.9	40.7	1.4	0.5	27.5
Max	2.9	6.7	95.9	7.6	5.9	79.9
Std. Dev.	0.4	1.9	24.2	1.8	1.5	15.3

9.8 Fermoy WWTP

Wastewater in Fermoy is collected in a partially combined and separate foul sewage drainage network. Fermoy WWTP is designed for a PE of 20,000 and a BOD loading of 1200 kg/day. Maximum hydraulic capacity of the plant is 673m^3/day which is 2.3 DWF, with additional storm storage provided. Originally built in 1987 for a design capacity of 9,000PE, the plant was recently substantially upgraded.

Influent, post inlet works and primary sedimentation, is now spilt 40% to original stream consisting of aeration phase in 2 No. oxidation ditches of volume 2700m^3 each, 3 No. θ13m secondary settlement tanks. 60% of the wastewater stream goes to the new process consisting of anaerobic, anoxic and aeration phase and secondary settlement in 1 no. θ 24m clarifier. Ferric sulphate is dosed at the aeration phase. Final effluent is discharged to the River Blackwater, designated sensitive waters under the Urban Wastewater Treatment Regulations (S.I. 254/2001).

Current population of Fermoy is now in excess of 2006 census figure of 5,800. Other sources of loading from industry, including an ice cream factory, auto components manufacturer, commercial premises, schools and tourism.

Figure 23. Fermoy WWTP
Scale 1:33416

Fermoy Results

	Influent			Effluent		
Sample Date	T-P mg/l P	MRP mg/l PO_4-P	% MRP/TP	Total mg/l P	MRP mg/l PO_4-P	%
16/08/2007				1.82	1.52	83.5
16/01/2008	3	2	66.7	0.4	0.3	75.0
07/02/2008	4.08	0.98	24.0	0.21	0.09	42.9
28/02/2008		1.8		0.37	0.36	97.3
26/03/2008		2.51				
03/04/2008	2.22	1.64	73.9	0.73	0.55	75.3
10/04/2008	6	2.5	41.7	1.3	1	76.9
12/06/2008	3.52	2.06	58.5	0.52	0.35	67.3
10/07/2008				0.48	0.39	81.3
15/07/2008	6	4	66.7	0.8	0.6	75.0
09/10/2008	8	2	25.0	2	0.6	30.0
19/02/2009	4.38	2.78	63.5			
05/03/2009		1.38				
Average	4.7	2.2	52.5	0.9	0.6	70.5
Min	2.2	1.0	24.0	0.2	0.1	30.0
Max	8.0	4.0	73.9	2.0	1.5	97.3
Std. Dev.	1.9	0.8	19.7	0.6	0.4	19.8

9.9 Kanturk WWTP

Kanturk is served by a separate foul and storm collection system. The wastewater treatment plant was constructed in 1994. Originally designed to cater for a PE of 3500, the 2006 Census puts the population at 1,915, and flow up to 4830m^3/day (6DWF) and 320 Kg/day BOD. Additional loading comes from tourism, commercial operations including a cattle market and a bakery and schools. Treatment consists of screening, flow is then spilt equally to 2 No. oxidation ditches, and 2 No. clarifiers. The final discharge is to the River Allow, a tributary of the Blackwater. There are no additional phosphorus removal measures.

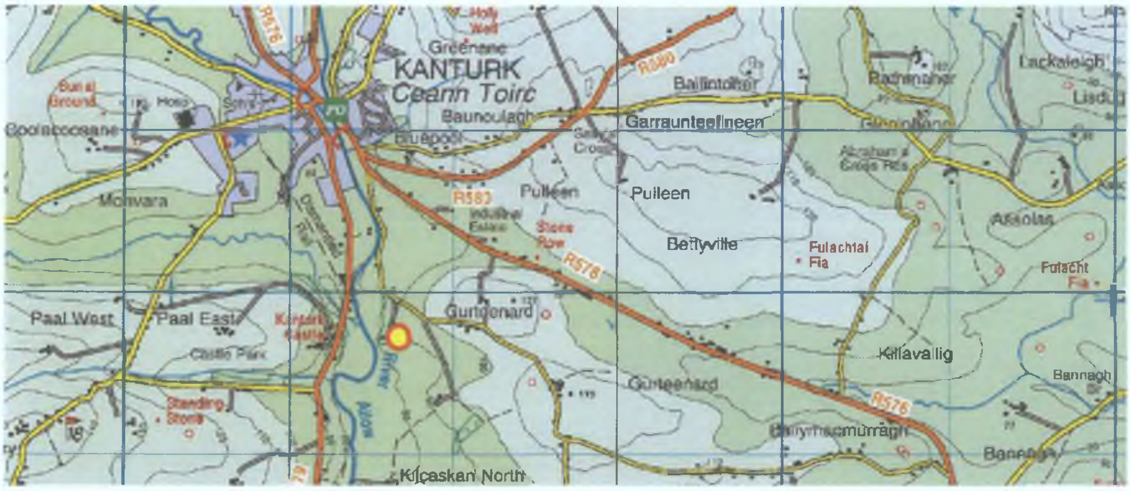


Figure 24. Kanturk WWTP
Scale 1:33416

Kanturk Results

	Influent			Effluent		
Sample Date	**T-P mg/l P**	**MRP mg/l PO_4-P**	**% MRP/TP**	**Total mg/l P**	**MRP mg/l PO_4-P**	**%**
21/08/2007	5.65	1.4	24.8	1.1	0.72	65.5
06/02/2008	1.5	0.9	60.0	0.7	0.5	71.4
14/02/2008	4.05	1.5	37.0	0.56	0.52	92.9
28/02/2008	1.95	1.41	72.3	1.11	0.97	87.4
03/04/2008	2.58	2.04	79.1	0.66	0.53	80.3
19/06/2008		1.98		2.28	2.08	91.2
17/07/2008	4.2	2.49	59.3	1.83	1.51	82.5
21/08/2008				0.56	0.5	89.3
05/09/2008	1	0.4	40.0	0.7	0.6	85.7
02/04/2009	6.55	3.55	54.2			
Average	3.4	1.7	53.3	1.1	0.9	82.9
Min	1.0	0.4	24.8	0.6	0.5	65.5
Max	6.6	3.6	79.1	2.3	2.1	92.9
Std. Dev.	2.0	0.9	18.4	0.6	0.6	9.2

9.10 Mallow WWTP

Current operating population equivalent for mallow WWTP is 13,000, which was designed to cater for high organic loadings from such industries as a Creamery and the sugar factory. The plant now has a design capacity of 18,000 PE, following a recent upgrade with hydraulic capacity 556m^3/hr at 2.5DWF and 1080kg/day BOD loading.

Following the upgrade, the influent is now split 50% to existing treatment, and 50% to the new works. Existing works consist of aeration phase, secondary settlement. The new stream utilizes the 'A^2/O' process for combined biological removal of phosphorus and nitrogen with anaerobic zones, anoxic zones and aeration. Ferric sulphate is also dosed at each of the aeration phases for additional phosphorus removal. Final discharge is to the River Blackwater, designated sensitive waters under the Urban Wastewater Treatment Regulations (S.I. 254/2001).

The domestic population of Mallow has grown over the past three censuses owing to its development as a town within the Cork Metropolitan Area. The most recent census has a population of 7091 (Census 2006). Other sources contributing to the loading include commercial premises, schools, tourism.

Figure 25. Mallow WWTP Scale 1:33416

Mallow Results

	Influent			Effluent		
Sample Date	T-P mg/l P	MRP mg/l PO_4-P	% MRP/TP	Total mg/l P	MRP mg/l PO_4-P	%
13/09/2007				1.46	1.22	83.6
16/01/2008	4	2	50.0	1	0.8	80.0
07/02/2008	4.48	1.64	36.6		0.29	
10/04/2008	7.95	3.95	49.7			
25/04/2008	8	4.2	52.5	1.8	1.8	100.0
13/06/2008				1.61	1.54	95.7
10/07/2008				1.3	1.23	94.6
21/08/2008				1.01	0.94	93.1
18/12/2008		2.36				
12/03/2009		2.33		1.33	0.64	48.1
02/04/2009	5.2	3.61	69.4			
Average	5.9	2.9	51.6	1.4	1.1	85.0
Min	4.0	1.6	36.6	1.0	0.3	48.1
Max	8.0	4.2	69.4	1.8	1.8	100.0
Std. Dev.	1.9	1.0	11.7	0.3	0.5	17.7

9.11 Middleton WWTP

Wastewater in Midleton is collected in a partially combined foul and surface sewer network. The WWTP is designed for a PE of 10,000 and a BOD loading of 600Kg/day, with maximum hydraulic capacity 90l/s (3DWF). Typical influent flows are 2DWF to 3DWF even during dry weather, suggesting a significant infiltration problem with the collection network, and which is currently undergoing an investigation and remediation project. The treatment process consists of inlet screening and maceration works, 8 aeration tanks of 406m^3 each, arranged in 2 lanes. The first aeration tank of each lane is not actually aerated and acts as an anoxic zone. Two 18.5m diameter final settlement tanks and finally UV disinfection on the final effluent. Treated effluent is lifted to a tidal holding tank at Rathcoursey fitted with a Lunar controlled penstock valve to discharge during tidal cycles to the Owenacurra River.

The pollution load for the Midleton WWTP arises from local population, Irish Distillers Group Ltd., Dawn Meats and Nordic Cold Storage. The population of Midleton as grown over the past few years. The 2006 Census has a population in excess of 10,000. The plant is currently undertaking an expansion to 15,000 PE with the addition of another lane of 4 aeration tanks with clarifier. The plant is currently the only wastewater works in County Cork >2000PE operated by a private contractor.

Figure 26. Midleton WWTP Scale 1:33416

Midleton Results

	Influent			Effluent		
Sample Date	**T-P** **mg/l P**	**MRP** **mg/l PO_4-P**	**% MRP/TP**	**Total** **mg/l P**	**MRP** **mg/l PO_4-P**	**%**
08/08/2007				0.47	0.2	42.6
05/09/2007	3.35	2.28	68.1	0.36	0.22	61.1
07/02/2008	1.66	0.78	47.0	1.09		0.0
28/02/2008		2.43		2.14	1.93	90.2
26/03/2008		3.57		1.31	1.18	90.1
07/04/2008		3.34		4.03	1.15	28.5
28/05/2008		4.17		4.4	2.41	54.8
12/06/2008	3.54	1.97	55.6	7	2.72	38.9
17/07/2008	4.93	4.15	84.2	5.45	1.35	24.8
07/08/2008				3.25	0.66	20.3
18/12/2008		1.71				
19/02/2009	2.45	1.42	58.0			
26/03/2009	4.09	2.48	60.6			
02/04/2009	2.36	2.08	88.1			
Average	3.2	2.5	65.9	3.0	1.3	45.1
Min	1.7	0.8	47.0	0.4	0.2	0.0
Max	4.9	4.2	88.1	7.0	2.7	90.2
Std. Dev.	1.1	1.1	15.2	2.3	0.9	29.4

9.12 Millstreet WWTP

Wastewater in Millstreet is collected in a partially combined foul and separate foul drainage network. The treatment plant, built in the early 1970's, is designed for a population equivalent of 1,600. Currently the plant is receiving an average DWF of 1,100 m^3/day and a BOD loading of 135 kg/day giving current load of 2,252 PE.

Treatment consists of a 53.4m x 11.95m x 1.3m extended aeration oxidation ditch and 2 No. hopper shaped settlement tanks. No preliminary treatment works are provided, and there are no additional phosphorus removal measures. Treated effluent discharges to the adjacent Tanyard Stream. A replacement plant with a design PE of 4,100 is due to be operational by 2011.

Figure 27. Millstreet WWTP Scale1:17509

Millstreet Results

	Influent			Effluent		
Sample Date	**T-P mg/l P**	**MRP mg/l PO_4-P**	**% MRP/TP**	**Total mg/l P**	**MRP mg/l PO_4-P**	**%**
21/08/2007				1.9	0.87	45.8
14/02/2008	4.75	2.43	51.2	3.93	2.3	58.5
19/03/2008	3.7	2.7	73.0	1.7	1.7	100.0
03/04/2008				1.79	1.45	81.0
23/10/2008				6.7	1.68	25.1
13/11/2008	21	13.16	62.7	1.5	1.03	68.7
19/11/2008	3	2	66.7	0.5	0.4	80.0
27/11/2008	16	8.22	51.4	1.1	0.99	90.0
05/03/2009	3.05	2.55	83.6			
Average	8.6	5.2	64.8	2.4	1.3	68.6
Min	3.0	2.0	51.2	0.5	0.4	25.1
Max	21.0	13.2	83.6	6.7	2.3	100.0
Std. Dev.	7.9	4.6	12.6	2.0	0.6	24.6

9.13 Mitchelstown WWTP

Wastewater in Mitchelstown is collected in a partially combined/separated foul sewage collection system. The wastewater treatment plant was originally built in early 1960's but refurbished in 1990. It is designed to cater for a PE of 6,000, although current loading is estimated at 4,100 PE. Treated wastewater is discharged to the Funshion River.

Treatment consists of 3 No. primary settlement tanks, 4 No. rotating biological filters and 8 No. humus tanks. A phosphorus removal plant was added in 2005, designed to remove 35.7 Kg/day phosphorus to give an effluent of 1mg/l total phosphorus by the dosing of ferric chloride at the primary sedimentation stage.

Figure 28. Mitchelstown WWTP
Scale1:17509

Mitchelstown Results

	Influent			**Effluent**		
Sample Date	**T-P mg/l P**	**MRP mg/l PO_4-P**	**% MRP/TP**	**Total mg/l P**	**MRP mg/l PO_4-P**	**%**
16/08/2007	2.25	0.87	38.7	1.97	0.74	37.6
16/01/2008	3	2	66.7	1	0.2	20.0
11/04/2008	3.7	2.8	75.7	2.1	1.1	52.4
15/07/2008	9	2	22.2	3	1	33.3
15/08/2008				3	0.4	13.3
09/10/2008	4	2	50.0	0.2	0.1	50.0
19/02/2009	4.38	2.08	47.5			
05/03/2009		0.92				
Average	4.4	1.8	50.1	1.9	0.6	34.4
Min	2.3	0.9	22.2	0.2	0.1	13.3
Max	9.0	2.8	75.7	3.0	1.1	52.4
Std. Dev.	2.4	0.7	19.2	1.1	0.4	15.7

9.14 Watergrasshill WWTP

Wastewater in Watergrasshill is collected in a partially combined foul and separate foul sewerage drainage network. The treatment plant ahs a design capacity of 3000 PE, although currently serves approximately 1600PE. Design DWF for the plant is $600m^3$/day.

Treatment consists of inlet works, θ7.8m extended air aeration tank, θ 5.3m settling tank, and 2 No. θ 1m sand filters. Final discharge is to the River Flesk. Ferric dosing is in place at the aeration tank for phosphorus removal. The plant is designed to achieve 10/10 BOD/SS standard.

Figure 29. Watergrasshill WWTP
Scale1:17509

Watergrasshill Results

	Influent			Effluent		
Sample Date	**T-P mg/l P**	**MRP mg/l PO_4-P**	**% MRP/TP**	**Total mg/l P**	**MRP mg/l PO_4-P**	**%**
16/08/2007	6.73	4.62	68.6	0.8	0.48	60.0
08/02/2008	4	2.3	57.5	0.9	0.2	22.2
08/02/2008	4	2.3	57.5	0.9	0.2	22.2
28/02/2008				2.15	2.05	95.3
20/03/2008				1.5	0.8	53.3
03/04/2008				2.42	2.06	85.1
04/06/2008	6.68	5.26	78.7	2.08	1.93	92.8
12/06/2008				1.1	0.95	86.4
10/07/2008				0.79	0.5	63.3
17/07/2008	7.98	4.66	58.4	1.07	0.66	61.7
20/08/2008	2.1	2	95.2	2	1	50.0
28/01/2009	4.95	3.08	62.2			
05/03/2009		4.37				
Average	5.2	3.6	68.3	1.4	1.0	62.9
Min	2.1	2.0	57.5	0.8	0.2	22.2
Max	8.0	5.3	95.2	2.4	2.1	95.3
Std. Dev.	2.0	1.3	14.1	0.6	0.7	25.6

10 Discussion and Conclusion

10.1 Discussion

10.1.1 Ballincollig

Highest result for influent total P was 16.2 mg/l on 02/04/09. The range of total P was from 3.9 to 16.2mg/l, with an average 11.6mg/l. MRP accounted for 60.2% of the total phosphorus. Highest influent MRP was 11.2 mg/l taken on the 05/06/08, accounting for 86.8% of the total phosphorus. The range of % MRP of TP-P was from 54 to 86.8%, with an average 64.3%. The high standard deviation 9.9 of % MRP/TP-P showed the fluctuation in results, reflected in the large range.

Effluent total phosphorus ranged from 4.6 to 8.1 mg/l with an average 6.4 mg/l, and lower standard deviation showing greater consistency in the effluent levels as opposed to the influent loadings. The highest value, 8.1 had a % MRP 86.4%.

10.1.2 Bandon

Highest result for influent total P was 8.8 mg/l on 17/07/08 with MRP accounting for 66.1%. The range of total P was from 3.8 to 8.8mg/l, with an average 5.5mg/l. Highest influent MRP was 5.78 mg/l was also taken on the 17/07/08. The range of % influent MRP of TP-P was from 51.9 to 78%, with an average 62.5%.

Effluent total phosphorus ranged from 1.4 to 5.1 mg/l with an average 3.7 mg/l, and lower standard deviation showing greater consistency in the effluent levels as opposed to the influent loadings. The highest value, 5.1 had a % MRP 83.8%. Effluent MRP ranged from 1.1 to 3.6 mg/l. The range of % MRP of TP-P was from 70.5 to 83.5 % with an average 78.4 mg/l.

10.1.3 Blarney

Highest result for influent total P was 12.6 mg/l. The range of total P was from 3.8 to 12.6mg/l, with an average 7.0 mg/l. Highest influent MRP was 6.4 mg/l taken on the 06/09/08. The range of % influent MRP of TP-P was from 44.3 to 87%, with an average 64.4%.

Effluent total phosphorus ranged from 0.6 to 2.2 mg/l with an average 1.6 mg/l, and very low standard deviation showing greater consistency in the effluent levels as opposed to the influent loadings as should be expected with phosphorus removal.

The highest value in effluent, 2.2mg/l had a % MRP 98.6%. Effluent MRP ranged from 0.5 to 2.2 mg/l. The range of % MRP of TP-P was from 85.9 to 98.6 % with an average 91.7 mg/l.

10.1.4 Castlemartyr

Highest result for influent total P was 33 mg/l, of which 37.7% was as MRP. The range of total P was from 4.8 to 33mg/l, for 4 samples with an average 14.2 mg/l. Highest influent MRP was 12.44 mg/l taken on the 05/09/07. The range of % influent MRP of TP-P was from 37.7 to 69.8%, with an average 53.9%.

Effluent total phosphorus ranged from 0.7 to 4.8 mg/l with an average 1.8 mg/l, with a very low standard deviation showing greater consistency in the effluent levels as opposed to the influent loadings as should be expected with phosphorus removal.

The highest value TP-P in effluent, 4.8 mg/l had a % MRP 95.5%. Effluent MRP ranged from 0.3 to 4.0 mg/l. The range of % MRP of TP-P was from 31 to 95.5 % with an average 70 %

10.1.5 Charleville

Low levels of phosphorus were found in Charleville influent. The range of total P was from 1.0 to 4.3mg/l, for 10 samples with an average 2.6 mg/l. Highest result for influent total P was 4.3 mg/l, of which 96.9% was as MRP. Highest influent MRP was 3.4 mg/l taken on the 02/04/09. The range of % influent MRP of TP-P was from 5% on the 09/10/08 to 96.9%, with an average 60%..

Effluent total phosphorus was consistently stable ranging from 1.1 to 2.0mg/l with an average 1.5 mg/l, with a very low standard deviation showing greater consistency in the effluent levels as opposed to the influent loadings as should be expected in a plant operating under capacity, even though there was no supplementary phosphorus removal. Effluent MRP ranged from 0.7 to 1.4 mg/l. The range of % MRP of TP-P was from 50 to 86 % with an average 72.5%l.

10.1.6 Clonakilty

Highest result for influent total P was 5.2 mg/l, of which 54.5% was as MRP. The range of total P was from 3.2 to 5.2 mg/l, for 4 samples with an average 3.9 mg/l. Highest influent MRP was 3.59 mg/l taken on the 19/06/09. The range of % influent MRP of TP-P was from 32.4 to 54.5%, with an average 43.5%.

Effluent total phosphorus ranged from 0.7 to 4.8 mg/l with an average 1.8 mg/l, with a very low standard deviation showing greater consistency in the effluent levels as opposed to the influent loadings as should be expected with phosphorus removal.

The highest value TP-P in effluent, 7.8 mg/l had a % MRP 98.1%. Effluent MRP ranged from 0.6 to 7.6 mg/l. The range of % MRP of TP-P was from 33.7 to 98.1 % with an average 73.1 %

10.1.7 Dunmanway

Highest result for influent total P was 2.9 mg/l, of which 95.9% was as MRP. The range of total P was from 1.9 to 2.9 mg/l with an average 2.3 mg/l. Highest influent MRP was 6.67 mg/l taken on the 19/06/08. There was no TP analysis. The range of % influent MRP of TP-P was from 40.7 to 95.9%, with an average 68%.

Effluent total phosphorus ranged from 1.4 to 7.6 mg/l with an average 3.1 mg/l. Surprisingly, average effluent TP-P and MRP levels were higher than average influent TP-P and MRP levels. The highest value TP-P in effluent, 7.6 mg/l had a % MRP 79.9%. Effluent MRP ranged from 0.5 to 2.0 mg/l. The range of % MRP of TP-P was from 27.5 to 79.9 % with an average 62.4.

10.1.8 Fermoy

Highest result for influent total P was 8.0 mg/l, of which 73.9% was as MRP. The range of total P was from 2.2 to 8.0 mg/l, with an average 4.7 mg/l. Highest influent MRP was 4.0 mg/l taken on the 15/07/08. The range of % influent MRP of TP-P was from 24 to 73.9%, with an average 52.5%.

As Fermoy discharges to sensitive waters, and is in excess of 10,000 PE, a total phosphorus limit of 2mg/l applies. Effluent MRP ranged from 0.6 to 1.5 mg/l. The range of % MRP of TP-P was from 30.0 to 97.3 % with an average 70.5 %

10.1.9 Kanturk

Highest result for influent total P was 6.6 mg/l, of which 79.1% was as MRP. The range of total P was from 1.0 to 6.6 mg/l, with an average 3.4 mg/l. Highest influent MRP was 3.6 mg/l taken on the 19/06/09. The range of % influent MRP of TP-P was from 24.8 to 79.1%, with an average 53.3%.

Effluent total phosphorus ranged from 0.6 to 2.3 mg/l with an average 1.1 mg/l.

The highest value TP-P in effluent, 2.3 mg/l had a % MRP 92.9%. Effluent MRP ranged from 0.5 to 2.1 mg/l. The range of % MRP of TP-P was from 65.5 to 92.9 % with an average 82.9 %

10.1.10 Mallow

Highest result for influent total P was 8.0 mg/l, of which 69.4% was as MRP. The range of total P was from 4.0 to 8.0 mg/l with an average 5.9 mg/l. Highest influent MRP was 4.2 mg/l taken on the 25/04/08 which accounted for 52.5% of the TP-P. The range of % influent MRP of TP-P was from 36.6 to 69.4%, with an average 51.6%.

Mallow wastewater treatment plant discharges to sensitive waters, so a 2mg/l limit for TP-P applies. Effluent total phosphorus ranged from 1.4 to 1.8 mg/l with an average 1.4 mg/l. On the 25/04/08, 100% of the TP-P discharged was as MRP.

10.1.11 Midleton

Highest result for influent total P was 4.9 mg/l, of which 84.2% was as MRP. The range of total P was from 1.7 to 4.9 mg/l with an average 3.2 mg/l. Highest influent MRP was 4.2 mg/l. The range of % influent MRP of TP-P was from 47 to 88.1%, with an average 65.9%. Midleton wastewater treatment plant discharges to sensitive waters, so a 2mg/l limit for TP-P applies. Effluent total phosphorus ranged from 0.4 to 7.0 mg/l with an average 1.3 mg/l.

10.1.12 Millstreet

Highest result for influent total P was 21.0mg/l, of which 83.6% was as MRP. The range of total P was from 3.0 to 21.0 mg/l with an average 8.6 mg/l. Highest influent MRP was 13.2 mg/l taken on the 13/11/08. The range of % influent MRP of TP-P was from 51.2 to 83.6%, with an average 64.8%.

Effluent total phosphorus ranged from 0.5 to 6.7 mg/l with an average 2.4 mg/l. Effluent MRP ranged from 0.4 to 2.3 mg/l. The range of % MRP of TP-P was from 25.1 to 100 % with an average 68.6.

10.1.13 Mitchelstown

Highest result for influent total P was 9.0 mg/l, of which 22% was as MRP. The range of total P was from 2.3 to 9.0 mg/l, with an average 4.4 mg/l. Highest influent MRP was 2.8 mg/l. The range of % influent MRP of TP-P was from 22.2 to 75.7%, with an average 50.1%.

Effluent total phosphorus ranged from 0.2 to 3.0 mg/l with an average 1.9 mg/l.
The highest value TP-P in effluent, 3.0 mg/l had a % MRP 52.4%. Effluent MRP ranged from 0.1 to 1.1 mg/l. The range of % MRP of TP-P was from 13.3 to 52.4 % with an average 34.4 %

10.1.14 Watergrasshill

Highest result for influent total P was 8.0 mg/l, of which 58.4% was as MRP. Average total phosphorus to the works was 5.2 mg/l. Highest influent MRP was 5.3 mg/l. The range of % influent MRP of TP-P was from 57.5 to 95.5%, with an average 68.3%.

Effluent total phosphorus ranged from 0.8 to 2.4 mg/l with an average 1.4 mg/l. The highest value TP-P in effluent, 2.4 mg/l had a % MRP 95.3%. Effluent MRP ranged from 0.2 to 2.1 mg/l. The range of % MRP of TP-P was from 22.2 to 95.3 % with an average 62.9%

10.2 Influent Discussion

Average phosphorus loadings were in the range 2.3 mg/l at Clonakilty to 14.2mg/l at Castlemartyr. Castlemartyr's high average influent TP-P (for n=4) samples was skewed by one sample of 33mg/l on the 05/09/07, a surprising result given that this wastewater treatment plant receives only domestic wastewater and light commercial wastewater from public houses, restaurants etc. A much more reliable upper end of the range for average influent TP-P in Cork is Ballincollig with 11.6 mg/l TP-P.

Average influent total phosphorus levels for County Cork's wastewater treatment plants are similar to those levels reported by Lie et al (1997) and Prochaska et al (2006) but generally lower than those reported by Dueñas et al (2002) and Akay et al (1998).

Average influent MRP ranged from 1.6 mg/l (Charleville) to 7.6mg/l (Ballincollig). Average MRP% of the total phosphorus ranged from 43.5% (Clonakilty) to 68 % at Watergrasshill and Dunmanway. Likewise % MRP of the TP-P is lower than that reported by Jolley et al 1998 who reported 86% of the total phosphorus of a sewage sample consisting of dissolved ortho-phosphate and Patel et al (2006) who reported orthophosphate accounting for 70.8 %.

Mainstone et al (2000) gives total phosphorus concentrations between 6 to 15mg/l depending on actual load, and the degree of dilution by clean water either by groundwater infiltration or storm water in combined sewers. It is clear from the range of results that the wastewater treatment plants are receiving significantly different phosphorus loading from the agglomeration served, as a result of type of discharges, type of sewer , i.e combined/separate and the actual integrity of the sewer to prevent the ingress of groundwater.

10.3 Effluent Discussion

Disregarding wastewater plants where supplementary phosphorus removal technologies were employed to comply with required standards under the Urban Waste Water Treatment Regulations, 2001(S.I No. 254 of 2001) average effluent concentrations of total phosphorus ranged from 1.1mg/l at Kanturk to 6.4mg/l at Ballincollig. Average effluent concentrations of MRP ranged from 0.9 to 4.6mg/l as P.

Removal of phosphorus at plants without additional phosphorus removal technologies was Ranged from 32.7 to 45%, in agreement with that reported by Balmer et al (1988), CEEP (1999) and Metcalf and Eddy (2003). The oxidation ditches at Kanturk and Millstreet achieved a good rate of removal with 67.6 and 72 % respectively. Although in comparison Ballincollig, using a similar process but being significantly overloaded, achieved a poorer rate of removal at 45% reflecting the overloading of the plant. Clonakilty likewise being overloaded achieved only 20% removal. Charleville, being under capacity, and receiving low levels of total phosphorus in the influent achieved 42% removal, but was able to consistently produce a good quality effluent without the need for additional chemical dosing.

For those effluents from wastewater treatment plants without chemical dosing, the % MRP of the TP-P discharged ranged from 62.4% at Dunmanway to 87.1% at Ballincollig. For plants with additional chemical dosing, the range was much broader, from 34.4% at Mitchelstown to 91.7% at Blarney.

10.4 Objectives Achieved?

1. Phosphorus, its extraction, uses and its environmental impact have been discussed, with particular emphasis on its impact on aquatic systems. The legislative measures to control phosphorus inputs to waters discussed, along with the techniques used to remove phosphorus from wastewaters.

2. I believe a little clarity has been brought to the terms used to describe phosphorus and its inorganic forms encountered in environmental monitoring. I hope the reader has a better understanding of the forms, the importance of the correct usage of them in environmental work and why confusion is arising. Section 7.2.2 demonstrates that SRP is not the same as MRP, and should not be used as interchangeable terms. The term orthophosphate should be avoided entirely as it may lead to confusion.

3. I believe there is little to support the 80% rule of thumb for orthophosphate as a percentage of the total phosphorus in a wastewater discharge. The range for plants without phosphorus removal was 62.4% to 87.1%, while the range was broader for plants with phosphorus removal, 34.4 to 91.7%. Percentage appears to be a function of type of treatment, and influent loading, and generalisations should be avoided. In any assimilative capacity assessment, the ability of the wastewater works to remove phosphate should be established from case studies.

11 Recommendations for future research

1. An investigation into the effectiveness of small scale on site wastewater treatment systems to remove phosphorus, and the level of compliance with planning permission conditions.

2. Investigate phosphorus load due to polyphosphates in an Irish context, and compare the amounts in smaller treatment plants with larger treatment plants where the collection network would be larger, allowing more time for breakdown of polyphosphates.

3. Establish whether the agreement between the Irish Detergent Industry Association and the Irish Government to eliminate STPP in detergents on the Irish marketplace by 2002 has been effective in reducing phosphorus loads to Irish wastewater works, or whether legislative measures are required.

4. Investigate ratio between influent phosphorus and organic carbon concentrations to ascertain whether EPBR can be enhanced at remote Irish wastewater plants, where there is no requirement to treat to the 2mg/l level, and the cost implications of retro fitting equipment as opposed to installation of chemical removal.

5. Investigate phosphorus composition of purely domestic wastewater without the addition of any industrial wastewater. The positioning of a refrigerated composite sampler in the sewer connection of a new housing development to the main sewer, and analysis of the various forms of phosphorus therein.

6. Investigate how the concentration of total phosphorus varies with rainfall events in combined and separate sewers. This would also provide an estimate of the dilution provided by groundwater infiltration during periods of dry weather when aquifer recharge rates are affected.

12 Glossary

Activated sludge treatment	Activated sludge is a process in sewage treatment in which air or oxygen is forced into sewage liquor to develop a biological floc, which reduces the organic content of the sewage.
Agglomeration	An area where the population and/or economic activities are sufficiently concentrated for urban waste water to be collected and conducted to an urban waste water treatment plant or to a final discharge point
Appropriate treatment	Treatment of urban waste water by any process and/or disposal system which after discharge allows the receiving waters to meet the relevant quality objectives and the relevant provisions of this and other Community Directives
Aquifer	Any stratum or combination of strata that stores or transmits groundwater.
Biochemical oxygen demand (BOD):	BOD is a measure of the rate at which micro-organisms use dissolved oxygen in the biochemical breakdown of organic matter in wastewaters under aerobic conditions. The BOD5 test indicates the organic strength of a wastewater and is determined by measuring the dissolved oxygen concentration before and after the incubation of a sample at 20°C for five days in the dark.
Buffer	A small area of permanent vegetation bordering a field, stream, or lake or running through cropland, protecting the soil from wind and rain erosion, slowing water runoff, and trapping sediment and other pollutants.
Coastal waters	The waters outside the low-water line or the outer limit of an estuary
Collecting system	A system of conduits which collects and conducts urban waste water
Constructed wetlands	A wetland system supporting vegetation, which provides secondary treatment by physical and biological means to effluent from a primary treatment step. Constructed wetlands may also be used for tertiary treatment as a 'polishing' step
Diffuse Pollution	Pollution which originates from various activities and which cannot be traced to a single source and originates from a spatially extensive land use (e.g. agriculture, transport)
Domestic waste water	Waste water from residential settlements and services which originates predominantly from the human metabolism and from household activities
Ecological Quality Ratio	An expression of the relationship between the values of the biological parameters observed for a given body of surface water and the values for those parameters in the reference conditions applicable to that body. The ration is expressed as a numerical value between zero and one, with high ecological status represented by values close to one, and bad ecological status by values close to zero.
Environmental Burden	A quantitative measure of the potential contribution of released substances to a particular environmental impact.
Environmental Quality Standard	Specifies the absolute compliance concentration or range for a water quality element in the environmental failure of which will be reported to the European Commission.
ELV	Emission Limit Value- the limit of a parameter allowed under a license or consent to discharge.
Epilimnion	Is the top-most layer in a thermally stratified lake, occurring above the deeper hypolimnion.
Estuary	The transitional area at the mouth of a river between fresh-water and coastal waters
Eutrophic	Systems that have a large supply of nutrients.
Eutrophication	The enrichment of water by nutrients, especially compounds of nitrogen and/or phosphorus, causing an accelerated growth of algae and higher forms of plant life to produce an undesirable disturbance to the balance of organisms present in the water and to the quality of the water concerned.
Hypereutrophic	Systems that have a very large supply of nutrients.

Hypolimnion	Is the dense, bottom layer of water in a thermally-stratified lake
Industrial waste water	Any waste water which is discharged from premises used for carrying on any trade or industry, other than domestic waste water and run-off rain water
Less sensitive areas	Marine water bodies or areas where the discharge of waste water does not adversely affect the environment as a result of morphology, hydrology or specific hydraulic conditions which exist in that area. When identifying less sensitive areas, Member States shall take into account the risk that the discharged load may be transferred to adjacent areas where it can cause detrimental environmental effects. Member States shall recognise the presence of sensitive areas outside their national jurisdiction. The following elements shall be taken into consideration when identifying less sensitive areas: open bays, estuaries and other coastal waters with a good water exchange and not subject to eutrophication or oxygen depletion or which are considered unlikely to become eutrophic or to develop oxygen depletion due to the discharge of urban waste water.
Mesotrophic	Systems that have intermediate nutrient supplies between Oligiotrophic and eutrophic
Molybdate Reactive phosphorus	Molybdate reactive phosphorus gets its name from the test used to determine the inorganic phosphorus species present in a sample.
Oligiotrophic	Systems with low supplies of nutrients, ie poorly nourished.
Organic matter:	Mainly composed of proteins, carbohydrates and fats. Most of the organic matter in domestic wastewater is biodegradable. A measure of the biodegradable organic matter can be obtained using the biochemical oxygen demand (BOD) test
Orthophosphate	Inorganic or soluble reactive phosphorus is usually called ortho-phosphate.
Population equivalent	population equivalent" is a measurement of organic biodegradable load and a population equivalent of 1 (1 p.e.) means the organic biodegradable load having a five-day biochemical oxygen demand (BOD5) of 60g of oxygen per day; the load being calculated on the basis of the maximum average weekly load entering the waste water works during the year, excluding unusual situations such as those due to heavy rain. May also be referred to as P.T in CEN standards.
Primary treatment	Treatment of urban waste water by a physical and/or chemical process involving settlement of suspended solids, or other process in which the BOD5 of the incoming waste water is reduced by at least 20% before discharge and the total suspended solids of the incoming waste water are reduced by at least 50%
Priority Substances	Substances identified in accordance with WFD Article 16(2) and listed in Annex X.
Riparian	Pertaining to the banks of streams, wetlands, lakes or tidewater.
River	A body of inland water flowing for the most part on the surface of the land, but which may flow underground for part of its course
River Basin District	Includes coastal/marine waters up to one nautical mile beyond the baseline from which territorial waters are measured. A river basin is the area of land from which all surface run-off flows through a sequence of streams, rivers and possibly lakes into the sea at a single river mouth, estuary or delta.
Salmonid waters	High quality waters suitable for the maintenance of viable self sustaining populations of wild salmon and trout, as defined by the Freshwater Fish Directive (78/659/EEC)
Secondary treatment	Treatment of urban waste water by a process generally involving biological treatment with a secondary settlement or other process in which the requirements established in Table 1 of Annex I of the Directive are respected
Sensitive areas	Freshwater bodies, estuaries and coastal waters which are eutrophic or which may become eutrophic if protective action is not taken; Surface freshwaters intended for the abstraction of drinking water which contain

	or are likely to contain more than 50 mg/l of nitrates; Areas where further treatment is necessary to comply with other Council Directives such as the Directives on fish waters, on bathing waters, on shellfish waters, on the conservation of wild birds and natural habitats, etc.
Sludge	Residual sludge, whether treated or untreated, from urban waste water treatment plants
Soluble Reactive Phosphorus	A measure of the inorganic phosphorus in solution. SRP is also called ‘Dissolved Reactive Phosphorus (DRP)’, ‘Dissolved Inorganic Phosphorus (DIP)’,
Storm water	The portion of precipitation that does not naturally percolate into the ground or evaporate, but flows via overland flow, interflow, channels or pipes into a defined surface water channel, or a constructed infiltration facility.
storm water overflow	means a structure or device on a sewerage system designed and constructed for the purpose of relieving the system of excess flows that arise as a result of rain water or melting snow in the sewered catchment, the excess flow being discharged to receiving waters.
Total Phosphorus	Concentration of the sum of organic and inorganic phosphorus.
Tertiary treatment	The final treatment stage to raise the effluent quality to the standard required before it is discharged to the receiving environment
Total Phosphorus	Total dissolved phosphorus plus particulate phosphorus
Trigger Action Value (TAV)	A numerical value proposed for some parameters, usually in parallel with an environmental quality standard (EQS) and which provides in these cases a more stringent non binding target than the EQS
Urban waste water	urban waste water" means domestic waste water or the mixture of domestic waste water with industrial waste water and/or run-off rain water.
Water Framework Directive	Directive 2000/60/EC of the European Parliament and of the Council of 23 October 2000 establishing a framework for Community action in the field of water policy
Water Policy Regulations	Irish Statutory Instruments which support the WD. EC Water Policy Regulations (SI 722 of 2003 and EC Water Policy Regulations (Amendment) (SI NO. 413 of 2005)
Wetlands	Those areas that are inundated or saturated by surface or ground water at a frequency and duration sufficient to support, and that under normal circumstances do support, a prevalence of vegetation typically adapted for life in saturated soil conditions. Wetlands generally include swamps, marshes, bogs, and similar areas.
WWTP	Waste water treatment plant

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