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5 **Effects of iron dosing used for phosphorus removal at wastewater**
6 **treatment works; impacts on forms of phosphorus discharged and**
7 **secondary effects on concentrations and fate of other contaminants**

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17

18 **Abstract**

19 Iron dosing for phosphorus reduction during wastewater treatment is wide practised across the
20 globe. However, the impacts of this dosing in terms of the speciation of phosphorus discharged and
21 secondary effects on removing or introducing other trace elements from or into the effluent, have not
22 been studied. Results are presented for concentrations of a range of contaminants in over 600
23 wastewater treatment works, reported as mean concentration values derived from 20 effluent
24 samples taken over a period of two years. Approximately half of the treatment works employed iron
25 dosing to reduce concentrations of phosphorus in effluents. In addition to the expected effects on
26 level of phosphorus discharged to surface waters, it is shown that these measures are shown to
27 have unintended and beneficial consequences for concentrations of several other constituents of
28 wastewater. Reductions of more than 40% in the concentrations of dissolved metals (copper, lead)
29 benzo(a)pyrene and hexabromocyclododecane are observed. Lower but still significant decreases
30 in concentration (>30%) are evident for dissolved cadmium, fluoranthene cypermethrin and
31 biochemical oxygen demand. Small but less environmentally important increases are seen for iron
32 and nickel, in the case of the latter this is presumably because nickel is a contaminant of the iron
33 reagent used for dosing. These reductions are shown to offer significant benefits in terms of levels
34 entering surface waters relating to the in-river environmental quality standards.
35

36

37 **Key words:** iron dosing; wastewater treatment works; priority chemicals; effluents; phosphorus;
38 trace elements

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40 **1. Introduction**

41 To meet increasingly stringent regulatory standards for the discharge of phosphorus to surface
42 waters (van Puijenbroeck et al 2019), water utilities across Europe have been progressively
43 extending phosphorus reduction measures at wastewater treatment works (WwTWs). Under the
44 European Union Urban Wastewater Treatment Directive, amongst other requirements, all
45 wastewater treatment works (WwTW) serving populations of greater than 10,000 need to achieve
46 an annual average total phosphorus concentration of <2 mg-P/l, Works serving populations greater
47 than 100,000 must achieve a <1 mg-P/l limit. For WwTWs discharging to very sensitive waterbodies
48 discharge limits of 0.1 mg-P/l are now being considered under legislation such as the Water
49 Framework Directive (WFD, 2000). Within Europe 64% of the population is served by WwTW
50 undertaking tertiary treatment, the vast majority of which apply chemical phosphorus removal (EU,
51 2000).

52

53 For example, in the UK on each day, approximately 347,000km of sewers collect 11 billion litres of
54 wastewater; this is treated in approximately 9,000 wastewater treatment works (WwTW) that serve
55 96% of the United Kingdom (UK) population (Cooper, 2014). WwTW effluents thus constitute by far
56 the most important discharges to surface waters and, consequently, are the principal source of
57 contaminant inputs to receiving river waters. The legislation has therefore led to marked reductions
58 in the discharge of the contaminants conventionally associated with sewage effluents, such as
59 biochemical oxygen demand (BOD), suspended solids and phosphorus. In more recent years,
60 however, there has been increased focus on a wider range of trace substance that did not feature in
61 the original design criteria of treatment processes. Current concerns, that are reflected in directives
62 such as the WFD, now extend to over 50 substances, including metals, pesticides, industrial
63 chemicals, solvents and other organic pollutants (EU, 2000). Reductions in concentrations of these
64 substances in wastewater are achieved by conventional treatment via biodegradation, volatilisation
65 or adsorption to sludge solids (Caravelli et al., 2012). Indeed, for some contaminants, removal
66 mechanisms can be highly effective (Gardner et al., 2013); in other cases, further or enhanced
67 treatment might be required.

68

69 The focus on phosphorus has led to a UK-wide Chemical Investigation Programme (CIP) with
70 monitoring at over 700 UK medium sized to large WwTW treating wastewater for a population of
71 over 20 million for phosphorus removal. Phosphorus removal is achieved by precipitation into
72 sewage sludge using iron salts in the vast proportion of cases (88%, 15.1 million people) (Bunce et
73 al., 2018; Cooper, 2014; Hauduc et al., 2015). In certain geographic areas such as the south west
74 of England and a few other specialised cases iron is substituted with aluminium salts (up to 33
75 WwTW, serving ~1million people) owing to its better efficiency in low alkalinity wastewater. In a few
76 limited cases (approximately 20 WwTW in UK serving ~5 million people) biological nutrient removal
77 is used where the crude wastewater supply is sufficiently phosphorus-rich to drive the microbial
78 processes required to effectively transfer the phosphorus into the sludge (Cooper, 2014). Even in
79 this case, however, chemical dosing may be required to meet the more stringent permits for
80 phosphorus discharges.

81

82 There has been reported research into the effectiveness of chemical dosing on effluent phosphorus
83 concentrations (Bunce et al., 2018; Caravelli et al., 2012; Comber et al., 2014) and recovery (Wilfert
84 et al., 2015) and in some cases impacts on sludge (Carliell-Marquet et al., 2019) and sulphide control
85 in sewers (Guitierrez et al., 2010). However, there has been an almost absence of widespread
86 examination of the impact of dosing either on forms of phosphorus (e.g. dissolved versus particulate),
87 or on the effect of removal on other contaminants. Any impacts of dosing on other priority chemicals
88 included in legislation are therefore of interest to WwTW operators and regulators alike.

89

90 Extensive monitoring over the past five years as part of the UK Water Industry Research (UKWIR)
91 Chemical Investigation Programme (CIP) has played a key role in the selection of substances and
92 sites for future controls and remedial measures (Gardner et al., 2012; Comber et al., 2014). The
93 most recent elements of the CIP have recently reported on effluent and river quality at over 600
94 sewage works in the period 2015-2020. This reporting (UKWIR, 2018) has focused on surface water
95 quality and compliance with environmental quality standards (EQSs) - the main purpose of that CIP.
96 It is also recognised that the CIP data provide a source of high-quality analytical data that can be
97 used to address other questions including the secondary effects of phosphorus. Analysis of the CIP
98 data set, specifically with respect to these objectives, has been carried out to characterise the effects
99 of dosing with respect to:

100

- **Effects of dosing on phosphorus speciation**

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Phosphorus speciation – to determine the relative proportion of soluble reactive phosphorus (SRP) to total phosphorus (TP) at sites with/without chemical P removal.

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- **Secondary effects of phosphorus treatment on concentrations of other substances**

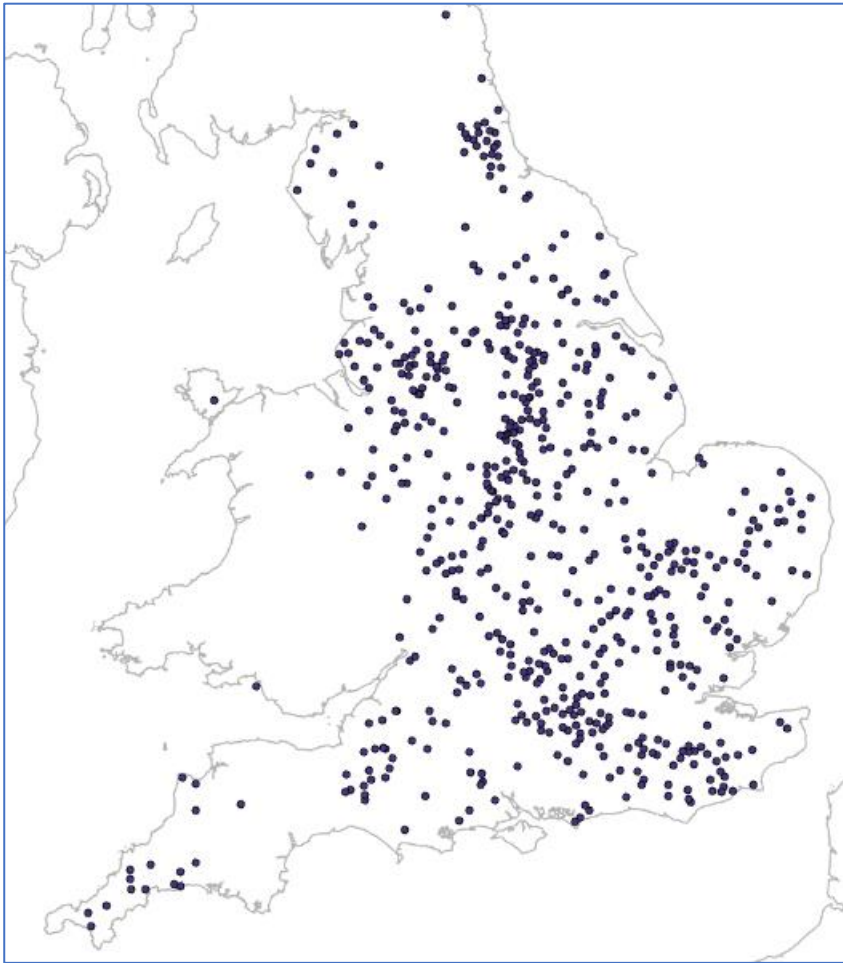
105 To assess the extent to which dosing can influence the concentrations of a number of trace
106 contaminants, including metals and trace organic substances that are of current interest in
107 effluents.
108

109 **2. Methodology**

110 **2.1 Sampling**

111 The results used here have been determined at 605 WwTW sites (20 per site in effluent and 36 per
112 site in river water upstream and downstream of the effluent discharge) over a period of five years
113 between 2015 and 2020 (Figure 1). Total numbers of samples therefore corresponded to over 12,000
114 for effluents and over 43,000 for river samples taken upstream and downstream of effluent
115 discharges. Stratified random sampling was conducted in four tranches of approximately two years'
116 duration each in order to capture a full set of within and between-year conditions.
117

118 Samples were collected on a stratified/random spot sampling basis (i.e. grab samples taken at
119 relatively evenly spaced times rather than multiple integrated sampling). A minimum of 15% of
120 sampling was undertaken in non-working hours (evenings and weekends).
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124 **Figure 1** Location of sampling sites for CIP2 WwTW used in this study

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126 **2.2 Sample treatment and analysis**

127 This topic is addressed briefly here; more background on the design and execution of the CIP
128 programme including the proficiency testing scheme, sampling protocols and determination of the
129 total and dissolved metal concentrations are given in the Electronic supporting Information (S1).
130 Briefly, water samples were collected in stainless steel samplers, stored in glass containers and
131 transported at 4° C to the analytical laboratories. Preliminary sample stability tests determined the
132 maximum sample storage period for key determinands. A period of 3 to 5 days storage for trace
133 determinands (depending on substance) was shown not to lead to more than a 25% change in
134 concentration. Analytical work was commissioned from laboratories with ISO17025 accreditation.
135 Prior to the programme candidate laboratories were required to undertake tests of analytical
136 performance to demonstrate that they met the stated programme requirements for limit of detection
137 (LOD), precision and recovery in relevant sample matrices at relevant concentrations (Table 1); that
138 is, proof of performance was required, rather than methods being stipulated.

140 **Table 1 Determinand required limits of detection and total error for WFD priority chemicals**

Substance and units (µg/l unless indicated otherwise)	Code	Concentration (µg/l)			P% ¹
		EQS	Required Limit of detection (effluent) ¹	Required Limit of detection (river water)	
nickel (dissolved)	NID	15	0.5	0.5	20
lead (dissolved)	PBD	8	0.2	0.2	20
copper (dissolved)	CUD	25	0.3	0.3	20
zinc (dissolved)	ZND	35	0.5	0.5	20
cadmium (dissolved)	CDD	0.25	0.04	0.02	20
iron (dissolved)	FED	1000	50	50	20
iron (total)	FET	730	50	50	20
aluminium (reactive)	ALR	50	4	4	20
Diethylhexyl-phthalate (DEHP)	DEHP	1.3	0.3	0.2	50
Brominated Diphenyl Ethers ("penta" congeners 28, 47, 99, 100, 153 and 154.) (BDEs)		0.0005	0.0005	0.0005	50
perfluorooctane sulfonic acid (PFOS)	PFOS	0.00065	0.00065	0.00009	50
perfluorooctanoic acid (PFOA)	PFOA	0.00065	0.00065	0.00009	50
Hexabromocyclododecane (HBCDD)	HBCDD	0.0016	0.0016	0.00023	50
tributyltin compounds (TBT)	TBT	0.0002	0.0002	0.00003	50
Fluoranthene	FLU	0.0063	0.0063	0.0009	50
benzo(a)pyrene (BaP)	BAP	0.00017	0.00017	0.00002	50
triclosan	TricI	0.1	0.1	0.014	50
cypermethrin	CYP	0.00008	0.00008	0.00001	50
total suspended solids (mg/l)	TSS		2	2	20
ammoniacal nitrogen (as N) (mg/l)	AMON		0.1	0.1	20
total oxidised nitrogen (as N) (mg/l)	TOXN		5	5	20
Biochemical Oxygen Demand (BOD) (mg/l)	BOD		2	2	20
Chemical Oxygen Demand (COD) (mg/l)	COD		10	10	20
Total phosphorus (as P) (TP) (mg P/l)	TP		0.01	0.01	20
soluble reactive phosphate (as P) (SRP) (mg P/l)	SRP	0.08	0.01	0.01	20

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142 ¹The target maximum tolerable error was set to be equal to:

143
$$\left[(targetLOD)^2 + \left(\frac{A \times P\%}{100} \right)^2 \right]^{\frac{1}{2}}$$

144

145 Where the target maximum LOD and P% are given in the table and A is the determinand
 146 concentration in the sample. Performance testing was designed to demonstrate that the tolerable
 147 total error limit is achieved by showing that precision (2 x standard deviation) and bias was
 148 respectively no larger than half the target maximum total error.

149

150 Within laboratory Quality Control (QC) analyses were undertaken for both laboratory tests and field
 151 sampling. Laboratories also took part in a bespoke proficiency testing scheme (see ESI S1).

152

153 **3. Results and discussion**

154 **3.1 Phosphorus – reactive and total phosphorus**

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156 This involved a comparison between the effluent quality of the CIP treatment processes that are not-
157 dosed and those that are dosed. This approach was enhanced by the fact that (by chance) the
158 comparison is one between almost exactly equal numbers (299 and 303) of dosed and not-dosed
159 sites. Effluents involving dosing with aluminium, of which there were only 25, were excluded on the
160 grounds that these would be too few to provide a worthwhile comparison. Soluble reactive
161 phosphorus (SRP) was defined by the phosphorus detected in a sample after filtration and analysis
162 by the phosphomolybdate method published by Murphy and Riley and formalised by the UK Standing
163 Committee of Analysts (Murphy and Riley, 1962, Standing Committee of Analysts 1992). Total
164 phosphorus (TP) was determined by either Inductively Coupled Plasma – Mass Spectrometry
165 (ICPMS) or by the molybdate method after rigorous digestion.

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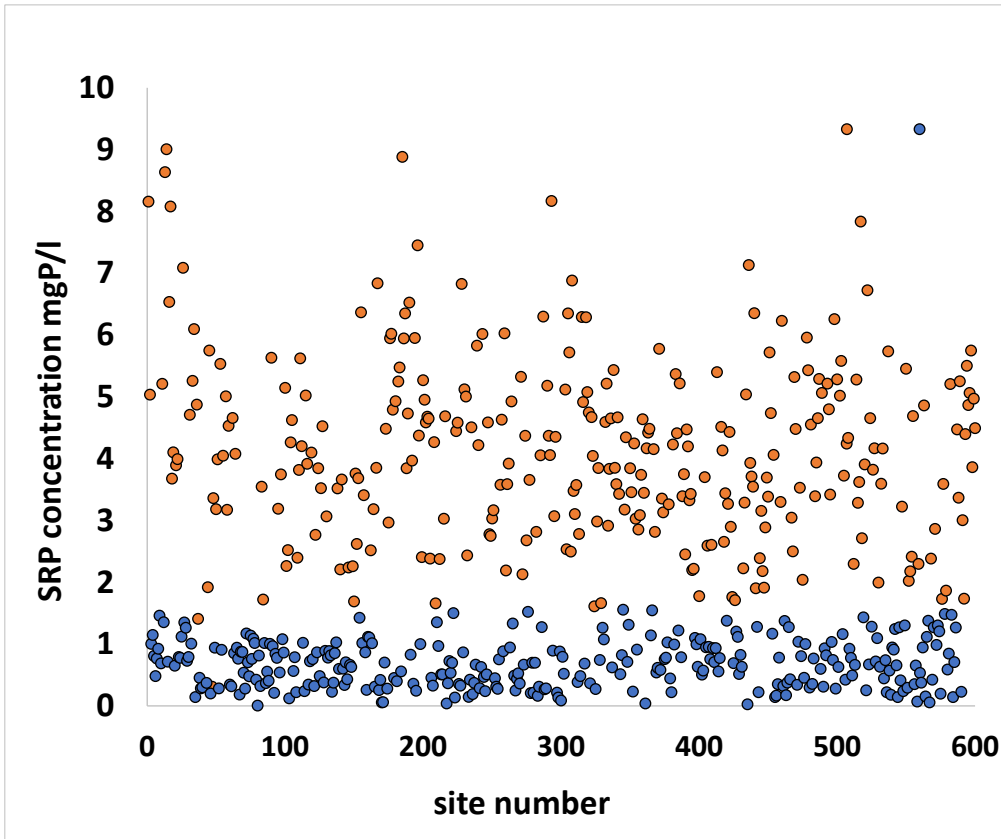
167 Figure 2 illustrates the clear distinction between the concentrations of SRP and TP concentrations
168 at dosed and not-dosed WWTWs. The reduction in mean TP concentrations resulting from dosing is
169 from 5 mgP/l to less than 1 mgP/l. The corresponding reduction in mean SRP values is from
170 approximately 4 mgP/l to less than 0.7 mgP/l, in both cases a reduction by a factor of five to six-fold.

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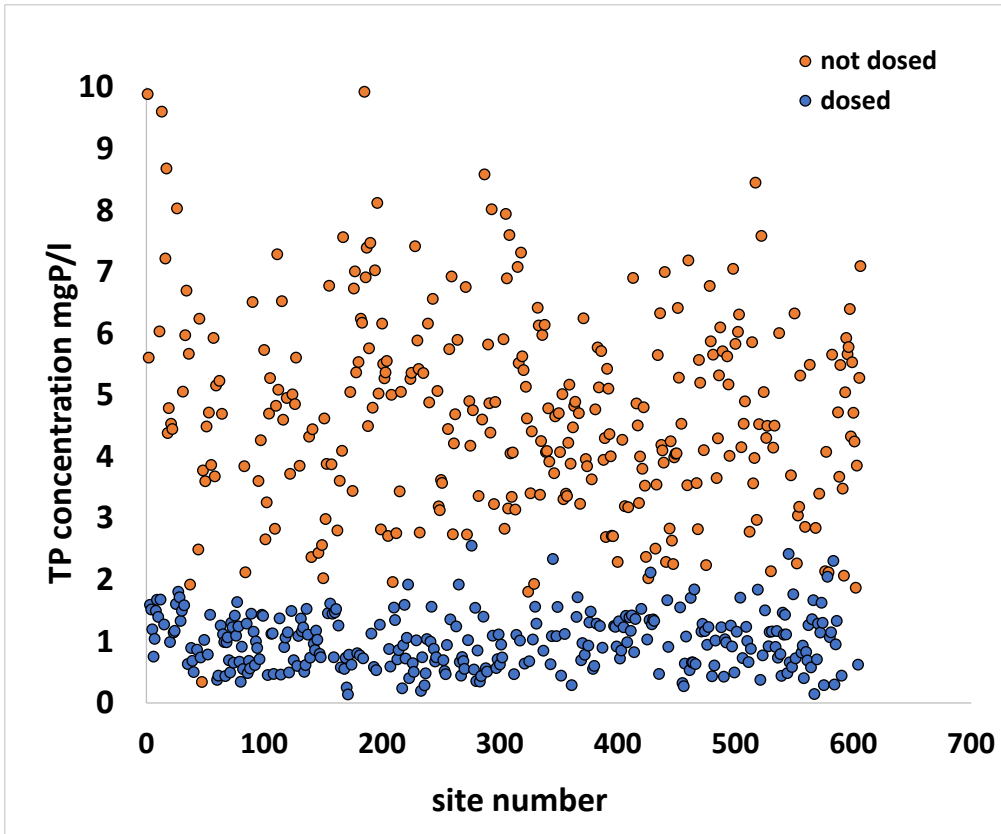
172 Figure 3 shows the effect of dosing on the proportion of SRP at dosed and not-dosed sites. Where
173 there is no chemical phosphorus reduction, this ratio is consistently in the range 0.75 to 0.95. Dosing,
174 however, results in a wider range of SRP/TP ratios, from as low as 0.3 to as high as 0.9. The reasons
175 for this range are not obvious from the data currently available, though measures including enhanced
176 effluent filtration and dosing regimens of increased sophistication are likely to be influential (Cooper,
177 2014). In as much as a third of cases the SRP/TP ratio is lower than 0.6; a potentially environmentally
178 important reduction on SRP over and above the reduction in TP that is achieved by dosing. In this
179 noteworthy proportion of cases the mean reduction in SRP concentrations is ten-fold or greater.
180 These data reflect the physico-chemical characteristics of the Fe (Al) flocculation process and its
181 influence on the phosphorus speciation, which may be modelled with sufficient data (Caravelli et al.,
182 2012; Hauduc et al., 2014).

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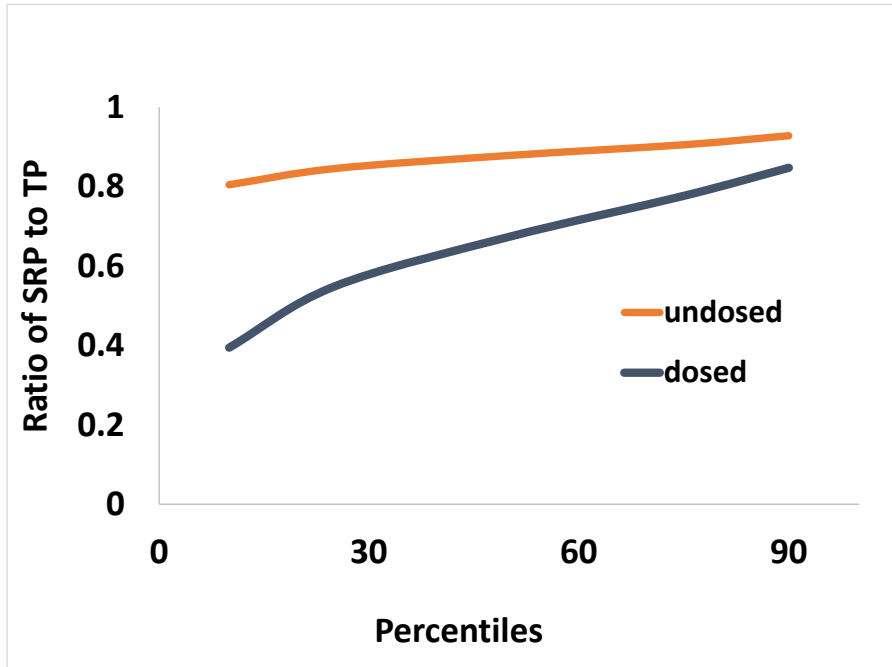


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Figure 2. SRP and TP concentrations plotted for all CIP2 sites

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193 **Figure 3. Ranges of the ratio of SRP to TP at dosed and not-dosed sites**

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195 **3.2 Secondary effects of chemical phosphorus reduction**

196 Differences in mean concentrations between dosed and not-dosed sites are shown in Table 1. Trace
197 determinands are listed at the top of the table, with sanitary parameters and iron lower down. The %
198 decrease values in bold. Negative values indicate an increase. Of these, for obvious reasons, only
199 iron stands out; the issues for nickel are discussed further below.

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Table 2 Differences in mean effluent concentration – not-dosed and dosed WwTWs

Determinand	Mean not-dosed (µg/l)	Mean dosed (µg/l)	Decrease (µg/l)	% Decrease in mean value	Student's t value	EQS value (µg/l)*	Not-dosed divided by EQS	Dosed divided by EQS
Soluble reactive phosphorus	4.1	0.7	3.4	83	39.9	0.067	62	10
Total phosphorus	4.7	1.0	3.7	79	38.9	n/a	n/a	n/a
HBCDD	0.0122	0.0059	0.0063	52	8.4	0.0016	7.6	3.7
Benzo(a)pyrene	0.0077	0.0040	0.0037	48	7.1	0.00017	45.1	23.4
DEHP	0.82	0.45	0.37	45	8.1	1.3	0.6	0.3
Dissolved copper	8.56	4.77	3.79	44	8.5	10.45	0.8	0.5
Dissolved lead	0.45	0.26	0.19	42	8.8	6	0.08	0.04
Cypermethrin	0.00048	0.00030	0.00018	38	3.5	0.00008	6.0	3.8
Fluoranthene	0.0144	0.0091	0.0053	37	6.5	0.0063	2.3	1.4
Biochemical oxygen demand	5.63	3.88	1.75	31	6.8	n/a	n/a	n/a
Dissolved cadmium	0.029	0.020	0.0089	30	6.4	0.08	0.4	0.3
Chemical oxygen demand	43	31	12	27	9.4	n/a	n/a	n/a
Dissolved zinc	29.5	23.0	6.57	22	5.3	24	1.2	1.0
Ammoniacal nitrogen	1.33	1.05	0.28	21	1.8	n/a	n/a	n/a
Total suspended solids	11.1	9.3	1.78	16	3.5	n/a	n/a	n/a
BDE47	0.00037	0.00032	5.182E-	14	5.2	0.0005	0.7	0.6
Tributyltin	0.00018	0.00017	0.000015	8	2.1	0.0002	0.9	0.8
BDE99	0.00032	0.00029	2.587E-	8	3.6	0.0005	0.6	0.6
Triclosan	0.068	0.067	0.0012	2	0.4	0.1	0.68	0.67
Total oxidised nitrogen	22.4	21.9	0.56	2	1.0	n/a	n/a	n/a
pH value	7.48	7.46	0.02	0	0.7	n/a	n/a	n/a
PFOA	0.0051	0.0055	-0.0004	-7	1.8	0.00065	7.9	8.5
PFOS	0.0045	0.0061	-0.0016	-35	4.5	0.00065	6.9	9.4
Dissolved nickel	2.4	4.5	-2.0	-84	11.5	14	0.2	0.3
Total iron	180	659	-479	-266	13.6			

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*EQS values for dissolved metal are site specific – these values are nominal based on a medium DOC water at pH 7.8

¹ PFOS results are anomalous because the results in the dosed data set were contaminated by a proportion of high “outlier” values.

It can be seen from the Student’s “t” values that the great majority of mean differences are statistically significant (p=0.05, double sided, for which where a critical t value would be approximately 2). This high level of significance is a consequence of having so many values from which to calculate each mean concentration. It shows that for all determinands (apart from PFOA, triclosan, total oxidised nitrogen and ammonia) a credibly real difference can be demonstrated. The question then is: “if there is a difference, is it of any practical importance”? This is addressed in the three columns on the right of Table 1, using the ratio of the effluent concentration to the relevant EQS value (where available) as guide to whether any likely change in concentration would be relevant in compliance terms. It should be noted that these data refer to effluents to be used as a rule of thumb, so the comparison

217 with the EQS value does not imply compliance status in the receiving water after dilution and across
218 the statutory assessment period. It should also be borne in mind that these data are overall mean
219 values and as we shall see below, within each data set the mean concentrations at individual works
220 are subject to variation around the mean.

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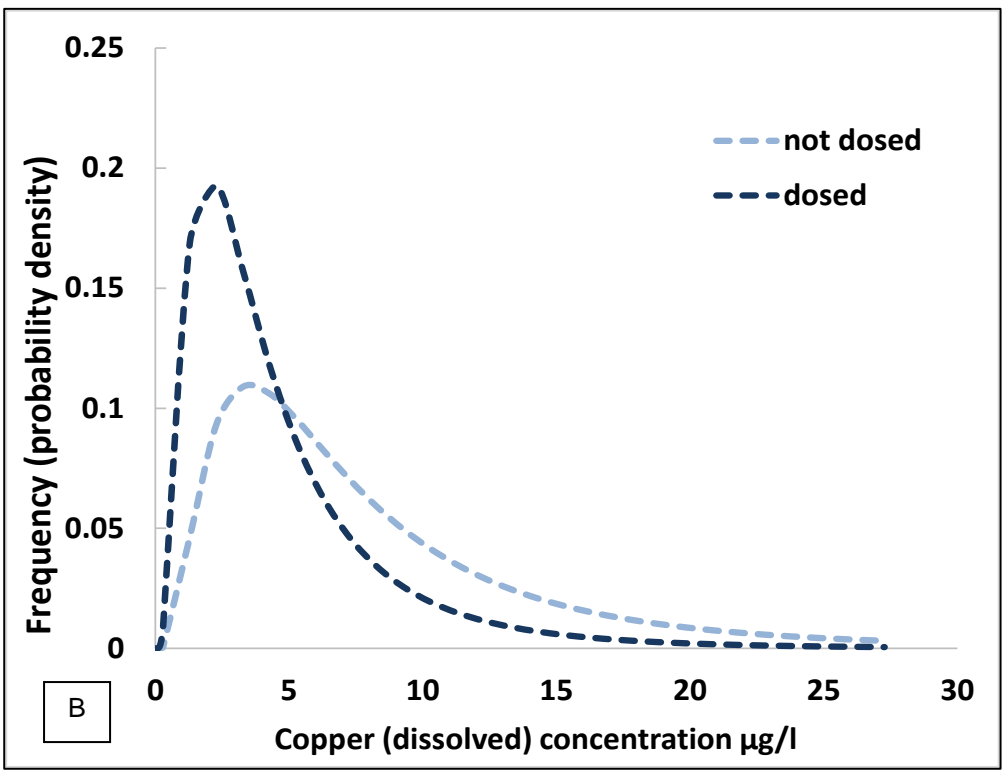
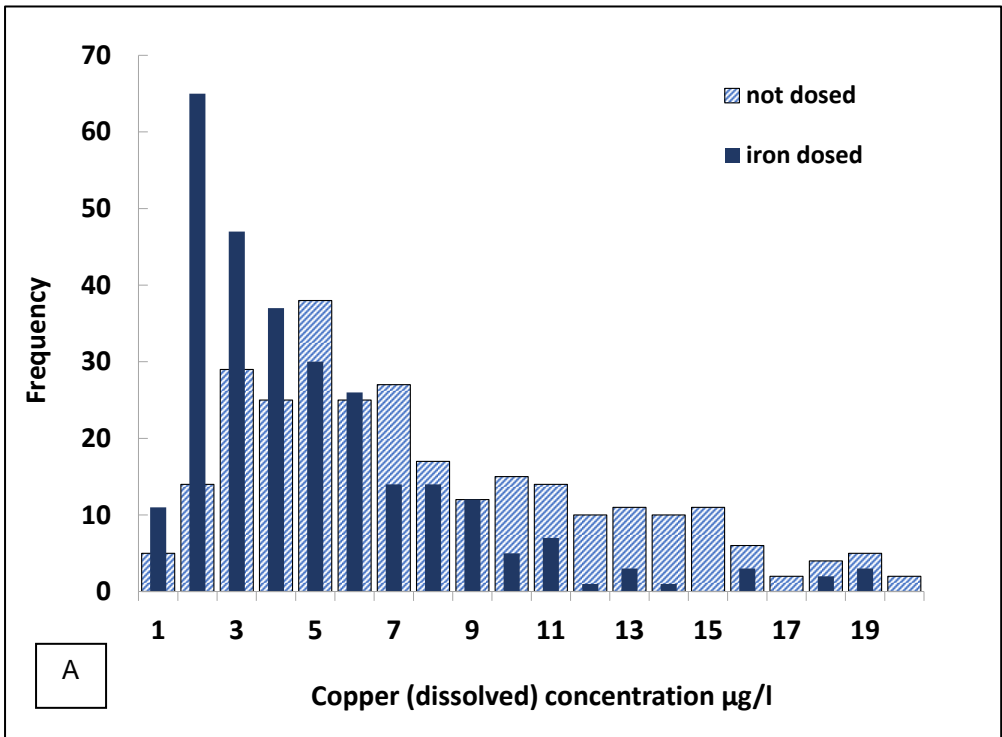
222 Several trace substances (the trace metals and phosphorus) are compared with a nominal EQS
223 value because the regulatory value varies with receiving water quality (EU 2013). In the last two
224 columns a ratio of less than one implies an effluent discharged at less than the EQS and a marked
225 change between the next to last and last indicates the extent to which dosing is associated with a
226 move in the direction of improved EQS compliance (and hence of potential relevance to contaminant
227 control). Having established that there are real and potentially important differences between dosed
228 and not-dosed effluent concentrations for several determinands of interest to the CIP (but not for all),
229 the next step is to consider the position for individual works and also the possibilities for sources of
230 difference that are not directly connected with dosing.

231

232 Figure 4A presents histograms for dissolved copper of mean results for individual WwTWs as a way
233 of visualising the distribution of values for the 300 or so effluents in each of the dosed and not-dosed
234 data sets. Similar histograms are presented for a further 21 determinands in the electronic supporting
235 literature (S2). In the case of copper, the x-axis is divided into concentration ranges 1 µg/l wide; the
236 y-axis shows the number of effluents having a mean value in each range. The not-dosed and dosed
237 histograms are superimposed for comparison purposes. From the Figure it is clear that the dosed
238 effluents (dark bars) occupy a range to the lower part of the plot where the not-dosed, lighter blue,
239 values are higher (to the right) as would be expected from the data in Table 1. The data, as previous
240 CIP experience suggests, are skewed to the right and closely correspond to a logNormal distribution.
241 The critical factor here is not only the change in mean concentration between dosed and not-dosed
242 WwTWs, but also the way in which the nature of the data distribution is changed. In this example,
243 and in many shown in ESI, S2, the essential issue is that for dosed WwTWs the profile is placed
244 lower in relation to not-dosed sites and is rendered somewhat less skewed. Both the mean and
245 standard deviation are reduced to result in an approximately similar coefficient of variation (CoV) for
246 both data sets. The consequence of this is that the incidence of works' mean concentrations in the
247 mid-range of the distribution are visibly reduced for copper.

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Figure 4. (A) Histogram of dissolved copper for dosed and not-dosed WwTWs and (B) Theoretical illustration of dosed and not-dosed copper pdf profiles

285 Figure 4B is a theoretical illustration of the case for dissolved copper, based on the respective
286 measured dosed and not-dosed mean and standard deviation values, displayed as a logNormal

287 distribution. The curves in Figure 4B follow the histograms in Figure 4A, but as a smoothed function.
288 The area under a given vertical slice of either one of the curves represents the probability of
289 encountering the set of concentrations bounded by the chosen slice. The whole area under both
290 curves is equal to one. The curves show that the way in which dosing modifies the effluent
291 concentration profiles. The key observation is that in the range (vertical slice) from approximately 8
292 $\mu\text{g/l}$ to approximately 18 $\mu\text{g/l}$ the area under the light blue not-dosed curve is larger (indicating a
293 probability of 0.31) than that under the dark blue dosed curve (probability = 0.13). Hence the
294 probability of finding a mean WwTW effluent concentration in this relatively elevated range for works
295 that are not-dosed is nearly three times that for sites which are dosed.

296

297 For dissolved copper, for which a nominal EQS of around 10 $\mu\text{g/l}$ (as dissolved metal) applies, the
298 number of sites where the risk of non-compliance might be important is markedly reduced. For any
299 determinand where this middle to high range of the distribution corresponds to the sites where EQS
300 compliance is limiting/borderline, this resulting benefit can therefore be substantial.

301

302 The electronic supporting literature (Figures S1 to S9) provides similar histogram outputs for the
303 other determinands in Table 1. In the case of some (total copper, HBCDD, Diethylhexylphthalate,
304 benzo(a)pyrene, fluoranthene, cypermethrin, dissolved cadmium, lead and zinc) the pattern
305 discussed above for copper is reproduced, though not necessarily quite so markedly. In other
306 instances (BDEs, PFOA, tributyltin, triclosan; Figures S10 to S14) there is little evidence for a dosing
307 related effect. With respect to the sanitary parameters total suspended solids and BOD shows a
308 small reduction in concentration from not-dosed to dosed (2 mg/l and 1.7 mg/l respectively; Figures
309 S15 and S16). The significant impacts on TP and SRP are clearly evident as would be expected
310 (Figures S19 and S20). It is worth noting that there is no difference evident for total oxidised nitrogen
311 or pH value (Figures S18 and S19) – two determinands for which an observed difference would defy
312 any mechanistic explanation of a dosing effect, if it had occurred. The sequence is completed (S20
313 to S23) with figures for phosphorus total iron and nickel.

314

315 In the case of copper in effluents, it is interesting to note that dosing seems to feature as important
316 in two ways. Firstly, there is the practice of adding phosphate to drinking water (typically between 1
317 and 2 mg/l), for the purpose of reducing the solubility of lead from domestic supply pipes - to ensure
318 compliance with the new WHO lead drinking water standard that was introduced in 2015 (Comber
319 et al., 2011, 2013). Then subsequently, there is the issue of dosing of wastewater to reduce
320 phosphate concentrations in sewage effluents. Tap water dosing has been reported as having an
321 accompanying effect of reducing the corrosion of copper pipes in domestic systems such that mean
322 tap water concentrations are lowered by around 40% from approximately 65 to 35 mg/l; the reduction

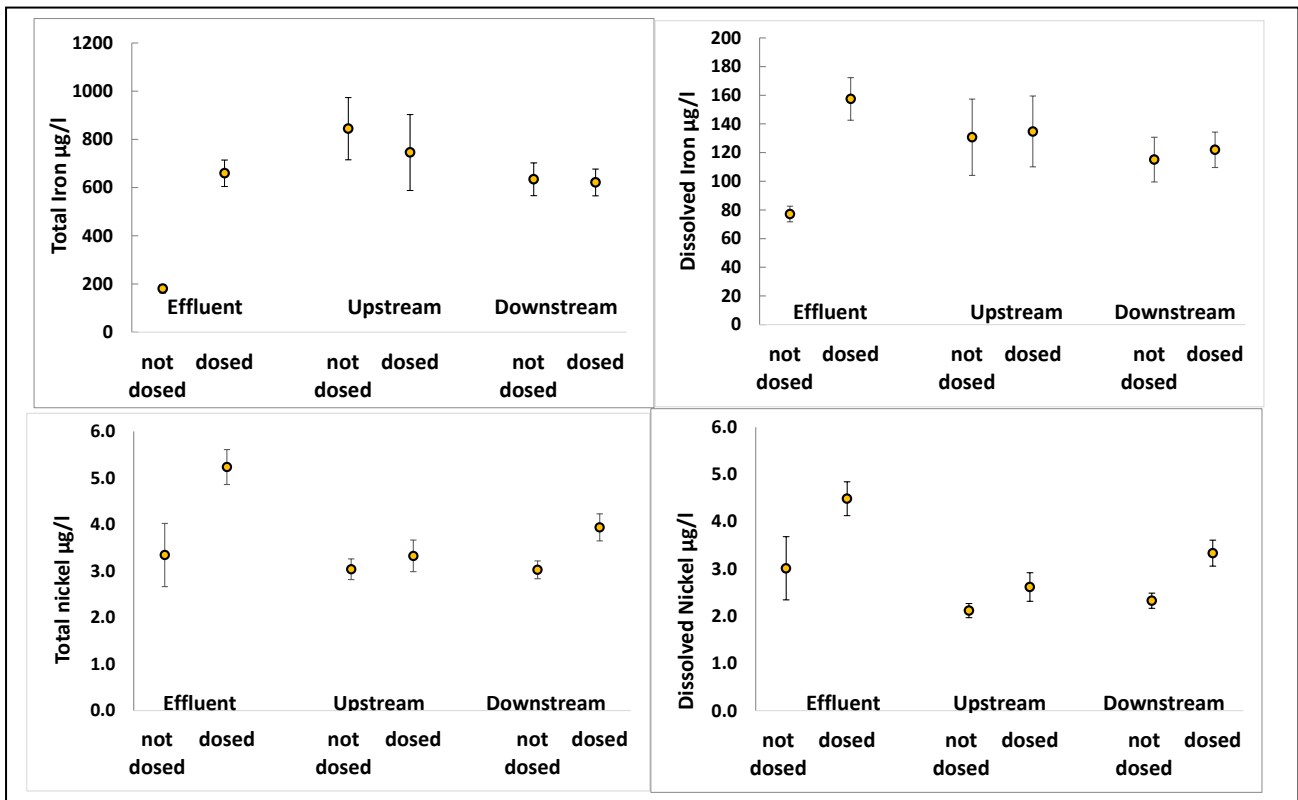
323 being proportional to the phosphate dose and shown to be reversible if phosphate dosing ceases
 324 (Comber et al., 2011). Given the results reported here, it might be that subsequently, as drinking
 325 water becomes wastewater, dosing for chemical phosphate reduction at WwTW will have a further
 326 suppressing effect on copper concentrations in effluent.

327

328 3.3 Iron and nickel in rivers and effluents - effect of dosing

329 Correlation between iron in WwTW effluents and nickel has drawn attention to the possible effects
 330 of chemical phosphorus removal on effluent quality and on the concentrations of these two metals
 331 in surface waters (Figure 5). The question posed here is what are the concentrations of the two forms
 332 of iron and of nickel and what kind of impact does dosing have downstream? The graphs below
 333 illustrate the findings that the CIP dataset provides. The upstream river samples were of course
 334 always not dosed – “dosing” here refers to what happens at the works site adjacent to the receiving
 335 water sampling point. These upstream values are shown as “controls” to illustrate comparability
 336 between the two groups of dosed and non-dosed sites.

337



338

339 **Figure 5. Comparison (mean and 90% confidence interval) between dosed and not-dosed**
 340 **data for effluent, upstream and downstream samples for total and dissolved iron**
 341 **and nickel**

342

343 The median and mean concentrations of dissolved iron in river waters in England and Wales are in
344 the range 60 – 120 µg/l. Concentrations of total iron tend to show more variability, around values of
345 500 - 600 µg/l (against an EQS of 1 mg/l as total iron). These concentrations are not observed to
346 change as a result of sewage effluent discharges, regardless of whether or not the effluent is dosed
347 with iron. This is likely to be a consequence of iron being a ubiquitous constituent of soils and
348 sediments, rather than what might be called an environmental pollutant. The fact that downstream
349 concentrations of iron (of either form) are not distinguishably different from those upstream provides
350 assurance that iron dosing is not having an overall measurable environmental impact and supports
351 the continued use of iron as a means of reducing phosphorus concentrations in effluents. It is worth
352 noting that these observations refer to the overall picture and that at individual sites there might be
353 the possibility of changes/effects that are not typical of the general case.

354

355 Mean concentrations of dissolved nickel in river waters in England and Wales are in the range 2.5-
356 3.5 µg/l. Mean concentrations of dissolved nickel in not-dosed effluent are also in this range. In the
357 population of effluents that are dosed with iron, the resulting effluent nickel concentration is increased
358 by an average of approximately 2 µg/l. The apparent effect of these discharges is to increase the
359 average downstream concentrations by approximately 1 µg/l. In all surface waters monitored in CIP,
360 whether the relevant effluent is dosed or not, very few instances of non-compliance with the nickel
361 environmental quality standard value are evident. The average concentration of total nickel is
362 between a half and 1 µg/l higher than that of the dissolved metal. The increase in total metal
363 concentration downstream of dosed effluent discharges remains at approximately 1 µg/l.

364

365 The example of nickel highlights the risks of dosing being a source of any contaminant (for example
366 zinc) that is present at significant concentrations in the dosing reagent. A further issue, though it is
367 outside the scope of this research, is the impact on secondary effects of the point in the treatment
368 process at which dosing is undertaken. Currently, the predominant approach is to dose early in the
369 process, thereby allowing the full period of treatment for precipitation reactions to occur. Later
370 dosing, possibly as a supplement, might mean that such processes have less time to take place with
371 consequent effects on effluent quality with respect to the dosing reagent. These are factors that
372 would need to be accounted for in any future development of dosing strategies.

373

374 4. Conclusions

375

376 Chemical phosphorus removal results in a reduction in mean total phosphorus (TP)
377 concentrations from 5 mg P/l to less than 1 mg P/l. The corresponding reduction in mean soluble
378 reactive phosphorus (SRP) values is from approximately 4 mg P/l to less than 0.7 mg P/l, a factor
379 of nearly six-fold. Where there is no chemical phosphorus reduction, the ratio of concentrations
380 of soluble reactive phosphorus SRP to TP is consistently in the range 0.75 to 0.95. Chemical
381 phosphorus removal results in results in a wider range of SRP/TP ratios from as low as 0.3 to as
382 high as 0.9. The reasons for this range are not evident from the data currently available, though
383 measures including effluent filtration and dosing of increased sophistication are likely to be
384 influential.

385

386 Comparisons of effluent quality for WwTWs where chemical phosphorus removal is applied show
387 clear and statistically significant improvements in quality for some unrelated determinands,
388 compared with sites where removal is not applied. Determinands affected in this way include
389 BOD, copper, HBCDD, DEHP, benzo(a)pyrene, fluoranthene, cypermethrin, dissolved cadmium,
390 lead and zinc. In other instances (BDEs, PFOA, TBT, triclosan, total oxidised nitrogen), there is
391 no evidence for a dosing-related effect.

392

393 It is not necessarily the case that chemical dosing is the sole reason for these changes in effluent
394 quality. These results are based on overall summary data that cannot isolate dosing as the sole
395 influencing variable. However, whilst other factors such a treatment works size and where
396 treatment is applied might have an effect, the data reported here are sufficiently clear as to
397 provide persuasive evidence that dosing does have an important part to play in the observed
398 effects reported here

399

400

401 An examination of the effects of dosing on receiving water quality downstream of dosed effluent
402 discharges indicates no overall effects for iron and only small, (> 1µg/l), increases in mean
403 concentrations for nickel.

404

405 The issue of gaining an improved understanding of the mechanism of some of the effects above,
406 whilst interesting, is secondary to the findings that the observed phenomena occur in the first
407 place. These dosing-related effects demonstrate that any changes, by reducing or widening the
408 used of iron-based phosphorus controls, could have unintended consequences with respect to
409 a range of other contaminants of separate and possibly equal concern. The characterisation of

410 mechanisms is also likely to be a difficult proposition because, various different driving processes
411 might be involved, in-situ investigations might be impractical and laboratory/pilot studies might
412 not be adequately realistic.

413
414

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420

421 **Conflicts of interest**

422 The authors no conflicts of interest associated with this research.

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