

Optimization of the water treatment process in an Italian winery: A case study

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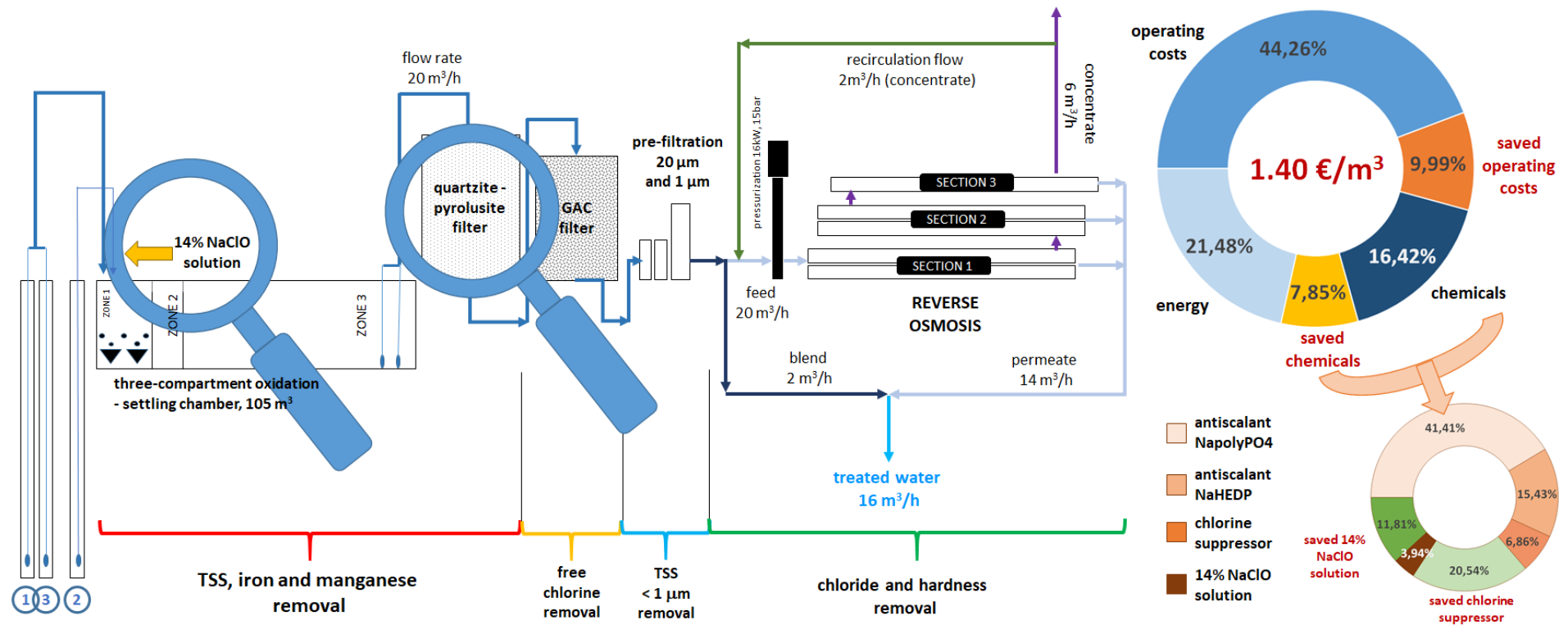
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Graphical abstract to the paper “**Optimization of the water treatment process in an Italian winery: a case study**”

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1 **Optimization of the water treatment process in an Italian winery: a case**
2 **study**

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26 **Abstract**

27 Water is an essential ingredient in wine production. The winery plant considered in this study, located in
28 the Langhe area (Piedmont, NW Italy), used approx. 100,000 m³ per year of high quality water for
29 cleaning and sanitation operations. Water was collected from the local shallow aquifer and contained
30 high concentrations of dissolved iron (Fe(II), 800 – 3,500 µg/L) and manganese (Mn(II), 300 – 700
31 µg/L). The water treatment plant (WTP) owned by the winery included a series of treatment processes
32 (air sparging and sodium hypochlorite injection, settling, filtration on a quartzite – pyrolusite filter,
33 removal of excess chlorine with an activated carbon filter and, finally, microfiltration and reverse
34 osmosis, RO) that were deemed to be adequate to make the groundwater compliant with potable uses.
35 However, a survey carried out by the authors revealed the presence of two critical issues in the WTP's
36 management, concerning the Fe(II) and Mn(II) oxidation and removal, and the backwashing of the dual
37 media filter. Firstly, the results of pilot tests demonstrated that the process of air sparging was sufficient
38 for the oxidation of iron and that NaClO was not necessary for that operation. The present concentration
39 of pure oxidant, of 21.5 mg NaClO/L, could be reduced by at least 75%, without altering the capacity of
40 the WTP in the removal of the two metals. Secondly, a new combination of water fluxes could improve
41 the efficiency of the dual media filter backwashing, thus allowing to simultaneously avoid the use of the
42 RO corrosive concentrate and to minimize the use of high quality water.

43 In the end, a very basic cost model was used to compare the unit cost for water treatment in the current
44 scenario and after the introduction of the two proposed solutions. Specifically, that model considered
45 three cost items: operating costs (that included four sub-items: mortgage, maintenance, consulting and
46 cost for non-amortizable raw materials and consumable), the costs for the purchase of the chemicals
47 necessary for the water treatment process, and the energy costs. The results coming from the application
48 of the cost model demonstrated that the introduction of the proposed solutions into the WTP, at no

49 additional costs, had an undeniable positive impact on the final unit cost of the treated water, that was
50 reduced by 20%.

51

52 **Keywords:** groundwater treatment; iron/manganese oxidation; dual media filtration; air sparging;
53 treatment cost; energy consumption

54 **1. Introduction**

55 The Langhe, a hilly area located in the Piedmont region (NW Italy), is well known for the production of
56 wines and sparkling wines, appreciated all over the world. That area was inscribed on the UNESCO's
57 World Heritage list in 2014. Even because of the recognized value of such an area, great efforts are
58 necessary to enhance the environmental sustainability of the wines' production processes.

59 Water, other than a precious natural resource for the survival and well-being of humans and the
60 ecosystem, is an essential ingredient in wine production. In fact, it must support grape-vine grown and
61 fructification in the field, and cleaning and sanitation processes of bottles and pieces of equipment in the
62 winery. Recent studies have revealed that the water footprint of wine was in the order of 800 liters of
63 waters/ L of wine [1]. That value came from both agricultural operations and winery processes; for the
64 latter ones, it was reported that the production of 1 liter of wine required 6 liters of water, with estimates
65 that varied from as little as 2 liters up to 20 liters [2-3]. Consequently, even in a winery, an efficient and
66 rationale usage of water is of primary concern to achieve a high degree of sustainability for wines'
67 production processes.

68 In most cases, the water used for cleaning and sanitation processes in a winery comes from a dedicated
69 water treatment plant (WTP), that collects raw water from the local deep or superficial water sources and
70 makes it suitable for the winery operations. In the case of the wine factory considered in this study, the
71 raw water came from a shallow aquifer and contained concentrations of dissolved iron, Fe(II), and
72 manganese, Mn(II), such high as to make it unsuitable for cleaning and sanitation processes, according
73 to the Italian regulation concerning the water intended for human consumption (D.Lgs. 31/01). In fact,
74 the concentration ranges of iron and manganese, in the raw groundwater used by the winery, were 800 –
75 3,500 µg/L and 300 – 700 µg/L, respectively, with respect to the threshold values of 200 µg/L, for iron,
76 and 50 µg/L, for manganese, fixed by D.Lgs 31/01. Iron and manganese are quite widespread in most of
77 the Italian groundwaters [4], both in the Langhe area and outside of the Piedmont region [5-6].

78 Iron and manganese in waters have been recognized as the cause of aesthetic and operating issues, such
79 as discoloration of water, staining of laundry and plumbing fixtures, metallic taste and odor, and scaling
80 of pipes [7]. Furthermore, recent studies reported that a manganese intake from water ingestion, even at
81 low levels, may lead to intellectual impairment in children [8] as well as other neurological disorders [9].
82 Ferrous iron can be oxidized quickly by oxygen under controlled conditions, particularly at alkaline pH.
83 Only occasionally, Fe(II) is complexed by natural organic matter (NOM) to the degree that oxygen is
84 unable to oxidize it in a reasonable time [10]. After oxidation, iron can be separated from water through
85 settling or granular media filtration [11].

86 Conversely, the conventional oxidation of Mn(II) through oxygen is very scarcely effective and the use
87 of free chlorine or other stronger oxidants presents a series of drawbacks: (i) free chlorine, even at pH
88 values of 8.0 or higher, required several hours of contact (and, consequently, large volume reactors) to
89 oxidize Mn(II); (ii) the oxidation efficiency of stronger oxidants, such as ozone or potassium
90 permanganate, depends on a series of factors, namely pH, temperature, initial dissolved manganese
91 concentration, contact time and presence of NOM; (iii) the presence of high concentrations of NOM
92 could cause pink water generation when potassium permanganate is used; (iv) the oxidation of Mn(II)
93 could form stabilized colloids, with a high negative charge, that are difficult to be separated by granular
94 filtration, but that could severely foul microfiltration or ultrafiltration membranes [12]. For all the above
95 listed reasons, specific treatments are required for the removal of Mn(II) from groundwater. It was
96 recognized that the combined processes of adsorption and oxidation of Mn(II) onto manganese oxide
97 (MnOx(s)) coated media, also known as “natural greensand effect” (NGE) process, was an effective and
98 economic method for Mn(II) removal. In the NGE process, Mn(II) is adsorbed onto the MnOx(s) coating
99 and then oxidized by chlorine at a neutral pH value, thus creating additional MnOx(s) [13]. The use of
100 pyrolusite as an adsorbing medium has shown a number of benefits in comparison with contactors
101 containing MnOx(s)-coated sand. In fact, pyrolusite is a natural manganese ore consisting of more than

102 80% MnO₂, it has high density of adsorption sites and finally, because of its specific gravity, in the order
103 of 5, it guarantees reduced particle entrainment and adequate media separation when a dual-media
104 granular filter (e.g. quartzite – pyrolusite) is used [14-15].

105 The WTP belonging to the winery considered in this study was originally designed and built with the
106 aim of removing iron, manganese and total hardness (due to the presence of high amounts of calcium
107 and magnesium into the groundwater), that made the collected groundwater not suitable for cleaning
108 processes of bottles, tanks and pieces of equipment. The WTP includes the processes of oxidation with
109 air and chlorine, settling, filtration on a granular dual-media (quartzite – pyrolusite) filter, removal of
110 excess chlorine through adsorption on an activated carbon filter and, finally, microfiltration and reverse
111 osmosis (RO). Even in the light of the considerations reported above, concerning the best techniques for
112 iron and manganese removal, the combination of the operations performed in the WTP was deemed to
113 be adequate for iron, manganese and total hardness removal. However, a survey carried out by the authors
114 on the WTP revealed the presence of some critical issues. Those issues seemed to be mainly related to
115 an apparent excessive amount of chemicals used for the treatment operations and to the maintenance of
116 the main pieces of equipment of the WTP.

117 Consequently, several survey campaigns were carried out to collect information concerning the quality
118 of the water at the inlet and at the outlet of the WTP, the characteristics of the pieces of equipment used
119 in the WTP, their energy consumption, and the type and amount of chemicals used for the water treatment
120 processes. The gathered information was used (i) to identify the critical issues connected to the water
121 treatment process, (ii) to propose solutions for the optimization of the process and, finally, (iii) to quantify
122 the economic impact coming from the introduction of the proposed solutions on the final unit cost of the
123 treated water.

124 **2. Materials and Methods**

125 **2.1 Groundwater quality**

126 The winery used approx. 100,000 m³ of water per year for operations of cleaning and sanitation of bottles,
127 tanks and pieces of equipment. The water demand of the winery was satisfied with the groundwater
128 collected from the local shallow aquifer through three wells, namely well n.1, n.2 and n.3. Well n.1 and
129 well n.3 were very close the one to the other; conversely, well n.2 was 50-m distant from wells n.1 and
130 n.3. The characteristics of the three wells are shown in Table 1.

131

132 Table 1. Characteristics of the three wells used to satisfy the water demand of the winery

Well identification	Depth (m)	Flow rate (m ³ /h)
1	25.0	13.5 (*)
3	22.5	
2	22.0	10.5

133 (*) sum of the flow rates from well n.1 and well n.3

134

135 Two pipes carried the groundwater from the wells to the inlet of the WTP. One pipe conveyed the mixture
136 of the groundwater collected from wells n.1 and n.3, the other pipe conveyed the groundwater collected
137 from well n.2.

138 The winery carried out periodic sampling campaigns at the outlet of each of the two pipes to monitor the
139 quality of the water conveyed by the two pipes separately. An external certified laboratory has assessed
140 the quality of the groundwater through the analysis of the following parameters: pH, electrical
141 conductivity (EC), chloride, sulfate, nitrogen compounds (ammonium, nitrite, nitrate), earth-alkali metals
142 (calcium, magnesium) and total hardness, metals and heavy metals (Fe, Mn, As, Cd, Cr, Hg, Ni, Pb, Cu,
143 Se) and biological parameters (total coliforms, *Escherichia Coli*, enterococci).

144 The results of the analyses carried out on the groundwater collected from wells n.1 and n.3, and from
145 well n.2, in the period 2015 – 2017, are detailed in Table 2. From the values of Table 2 it can be seen
146 that iron and manganese were the most critical compounds, because their concentrations exceeded the
147 threshold values fixed by Italian D.Lgs. 31/01 in almost all of the sampling dates. In fact, the
148 concentrations of iron and manganese in the groundwater from wells n.1 and n.3 were 3-4 times higher
149 than the threshold values (of 200 and 50 µg/L, respectively) and those in the groundwater from well n.2
150 were even 15-20 times higher. Furthermore, the quality of the groundwater collected from wells n.1 and
151 n.3 was, on average, superior to that collected from well n.2. Specifically, the average (2015-2017)
152 concentration of iron in well n.2 was five times higher than that found in wells n.1 and n.3 (3306 µg/L
153 vs. 634 µg/L) and the concentration of manganese was two times higher (611 µg/L vs 322 µg/L). Finally,
154 the concentrations of iron and manganese in the two wells in the last two years (2016-2017) were at
155 almost constant values.

156 Other than iron and manganese, also chloride and total hardness deserved special attention. In fact, the
157 average concentration of chloride was 193 mg/L, in wells n.1 and n.3, and 207 mg/L, in well n.2,
158 respectively, while the threshold value was at 250 mg/L. The average total hardness was approx. 51 °F
159 in wells n.1 and n.3 and of more than 60 °F in the waters of well n.2. There are no threshold values for
160 total hardness fixed by the Italian law that regulates drinking water, but the groundwater of that site was
161 found to be very hard, thus exceeding the upper limit of the range (15 – 50 °F) recommended for
162 household or industrial uses.

163

164 **2.2 Water treatment plant description**

165 The WTP owned by the winery was originally designed with the aim of removing those compounds,
166 namely iron, manganese and earth-alkali metals (calcium, magnesium), that made the collected
167 groundwater not suitable for household or industrial uses. The yearly average volume of the water treated

168 in the WTP was in the order of 130,000 m³. The winery employed the treated water chiefly for the
169 washing processes of bottles, tanks and pieces of equipment. Small amounts of water were also used for
170 spirit production and for the cooling circuits; that water required advanced treatments in order to achieve
171 the quality necessary for the specific uses.

172 The scheme of the WTP is shown in Figure 1. The groundwater conveyed by the two pipes is mixed at
173 the inlet of the WTP and added with a 14% b.w. (by weight) solution of sodium hypochlorite (NaClO).
174 The NaClO solution is supplied to provide a preliminary disinfection and to facilitate the oxidation of
175 iron and manganese.

176 Subsequently, the water remains into a three-compartment chamber, with a total volume of 105 m³,
177 located under the floor of the WTP's premise. The first compartment has a volume of approx. 20 m³; a
178 total of 14 membrane air diffusers (Jager HD270, 270 mm diameter) are regularly distributed at 40 cm
179 from the bottom of the tank. The diffusers distribute air into the water at a volumetric flow rate of 100
180 m³/h through a 1.5 kW blower. The air sparging should improve the oxidation of iron(II) to iron(III)
181 oxide, Fe₂O₃, and allow the subsequent removal by settling. The first compartment has a hydraulic
182 retention time (HRT) of 50 minutes at a flow rate of 24 m³/h. The two subsequent compartments have
183 volumes of 14 m³ and 72 m³, respectively. These two tanks are used as settling chambers to allow iron
184 oxides be removed by settling. The average HRT of the two compartments was of 35 minutes and 3 hours
185 respectively at a flow rate of 24 m³/h.

186 From the third compartment the water is pumped to a close, pressurized, dual media granular filter. The
187 filter has a volume of 4 m³, 70% of which is filled with the granular media. The two media are quartzite
188 and pyrolusite. Quartzite granules are supplied in two different size ranges, that is 3-5 mm and 0.8-1.2
189 mm. Pyrolusite, a manganese oxide (MnO₂, ρ = 5.06 g/cm³), is used to remove manganese through the
190 combination of the processes of adsorption of Mn²⁺ on the pyrolusite surfaces and subsequent oxidation
191 of the adsorbed species by chlorine [10, 16]. A granular activated carbon (GAC) filter follows the dual

192 media filter. The GAC filter is used to remove the residues of active chlorine (in the form of hypochlorous
 193 acid, HClO), that results from the addition of the NaClO solution, and protect the final section of the
 194 WTP, where a RO process is carried out. The GAC filter has a volume of 3 m³ and it is filled with 800
 195 kg of 30-8 mesh vegetal GAC. The WTP managers did not consider the GAC filter sufficient to guarantee
 196 a complete chlorine removal for the protection of the RO section. Consequently, even chlorine suppressor
 197 agents, such as sodium bisulfite (NaHSO₃), are currently used to remove residual amounts of active
 198 chlorine.

199 The two dual media and GAC filters are regularly backwashed, that is after the passing of 600 m³ of
 200 water (i.e. 30 hours). The phases of the backwashing operation are detailed in Table 3.

201

202 Table 3. Phases of the backwashing operation carried out on the dual media and GAC filters

Filter	Phase 1 Air	Phase 2 RO concentrate	Phase 3 Water from the third compartment (*)
Dual media	70 m ³ /h	YES	45 m ³ /h
GAC	40 m ³ /h	NO	25 m ³ /h

203 (*) of the tank used for air sparging and settling

204

205 A section of pre-filtration precedes the final RO. The pre-filtration stage is composed of a first series of
 206 two 20 µm polypropylene cartridge filters and a subsequent 1 µm polypropylene cartridge filter. The RO
 207 section is made of 5 fiberglass vessels, each of them contains 3 thin-film composite, polyamide, spiral-
 208 wound membranes (RE8040-BLR). The RO section produces, on average, 14 m³/h of permeate and 6
 209 m³/h of concentrate. Approximately 2/3 of the concentrate is stored in a 35 m³ reservoir and used for the
 210 dual media filter backwashing. The remaining amount of concentrate (2 m³/h) is recirculated back and
 211 mixed with the water that comes from the section of pre-filtration. A value of total dissolved solids

212 (TDSs) of 500 $\mu\text{S}/\text{cm}$ at the outlet of the RO section is guaranteed thanks to the blending of the permeate
213 ($14 \text{ m}^3/\text{h}$) with an amount of water ($2 \text{ m}^3/\text{h}$) that comes from the outlet of the pre-filtration section.
214 The recirculating amount of the concentrate is added of two antiscalc compounds before being mixed
215 with the water coming from the pre-filtration section. The two antiscalc compounds are in the form of
216 sodium polyphosphate (25-40%) and a mixture of etidronic acid ($< 5\%$) and di-hydrogen (1-hydroxy-
217 etilden) di-sodium phosphonate ($>10\%$). The RO membrane regeneration process is carried out through
218 periodic chemical cleanings with alkali (sodium hydroxide plus surfactant) and acidic ($\text{C}_6\text{H}_8\text{O}_7$, citric
219 acid) solutions.
220 A final chlorination with NaClO guarantees the complete inactivation of pathogenic microorganisms.
221 The disinfected water is stored in a 124 m^3 reservoir for end uses or subsequent enhanced treatments.

222

223 **2.3 Water treatment plant survey**

224 Wine production is a seasonal activity, for that reason several survey campaigns were carried out on the
225 WTP in different moments of the year. Surveys were aimed at collecting information concerning the
226 quality of the water at the inlet and at the outlet of the WTP, the characteristics of the pieces of the
227 equipment of which the WTP is composed (as described in Section 2.2), their energy consumption, and
228 the type and amount of chemicals used for the water treatment processes.

229 The information acquired from the surveys was used (i) to identify the critical issues connected to the
230 water treatment process, (ii) to propose solutions for the optimization of the process and, finally, (iii) to
231 quantify the economic impact of the introduction of the proposed solutions on the final unit cost of the
232 treated water.

233 **2.4 Tests for WTP optimization**

234 After having identified the main WTP's critical issues, tests were executed to optimize the water
235 treatment process. One test was carried out with the aim of assessing the amount of oxidant (14% NaClO
236 solution) necessary for iron and manganese oxidation.

237 The test was performed on a sample of real water collected at the inlet of the WTP. A volume of 10 liters
238 of the mixture of the two ground waters coming from wells 1+3 and 2 was collected in a polypropylene
239 tank. The test was articulated in five steps: (1) analysis of the main parameters (ORP, Fe, Mn, free
240 chlorine) of the collected water sample; (2) distribution of an air flow (50 L/h) into the water volume
241 through porous stones for approx. 50 minutes (i.e. the air flow was consistent with the flow provided by
242 the membrane air diffuser to the first compartment of the oxidation – settling chamber and 50 minutes
243 was the HRT of the compartment, see Figure 2a); (3) analysis of the parameters, listed in step (1), in the
244 water sample after the aeration treatment. The residual concentrations of iron and manganese were
245 determined after filtration on a 0.45 µm cellulose-acetate filter (Sartorius, CA syringe filters, 25 mm
246 Ø), in order to quantify only the concentration of the metals in the dissolved, not oxidized, form, as
247 prescribed by Standard Methods (APHA, AWWA, WEF, 2017) [17]; (4) mixing of the water volume
248 after the aeration with three in-sequence doses of NaClO: 4 mg/L, 10 mg/L and 40 mg/L. The contact
249 time between water and oxidant, after the addition of each dose, was of 30 minutes; the oxidant was
250 vigorously mixed with the water at the beginning and subsequently the water was left still; (5) analysis
251 of the parameters listed at step (1) in the water sample after each of the contact periods for the three
252 above-mentioned oxidant doses. As in step (3), the residual concentrations of iron and manganese were
253 determined after filtration on a 0.45 µm cellulose-acetate filter. The test was repeated three times.
254 Concentrations of iron, manganese and residual free chlorine were determined immediately at the end of
255 each test step with rapid analytical kits (Reasol IPT, see Figure 2b).

256 **2.5 Water treatment cost analysis**

257 The cost data used for the quantification of the unit cost of the treated water were obtained from the WTP
258 survey campaigns mentioned in Section 2.3. The cost analysis considered a period of ten months, from
259 June 2017 to March 2018. As in previous works [18-19], the overall unit cost for the treated water was
260 calculated by including the cost items listed in the follow:

- 261 • Amortization installments for the replacement of pieces of equipment (such as membranes for
262 microfiltration and RO) and purchase of raw materials for filter unit filling (quartzite, pyrolusite,
263 granular activated carbon). Amortization installments (AI) were calculated by multiplying the
264 costs of the pieces of equipment and raw materials (TC) by the capital charge rate (CCR), as in
265 Equation (1)

266

267
$$AI = TC \cdot CCR = TC \cdot \frac{i}{1-(1+i)^{-n}} \quad (1)$$

268

269 The annual interest rate (i) and the operating life (n) were fixed to 5% and 3 years, respectively.

- 270 • Operating costs for maintenance, consulting, energy, raw materials and consumable (specifically
271 for the chemicals employed in the water treatment process) [20].

272 **3. Results and Discussion**

273 **3.1 Critical issues' identification**

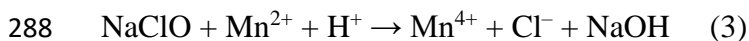
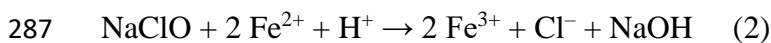
274 The first critical issue detected from the WTP's survey was an apparent excessive amount of NaClO
275 solution employed for the water treatment and, specifically, for iron and manganese oxidation. In the
276 WTP, the NaClO solution is added to the raw water immediately after the mixing of the two flows, before
277 the water enters into the three-compartment chamber used for aeration and settling (see Section 2.2).

278 The analysis of the cost data revealed that the amount of the 14% NaClO solution purchased from June
279 2017 to March 2018 was of 15,000 kg. In the same period the volume of the treated water was of 97,600
280 m³, consequently, the dose of the pure oxidant distributed to the water was of 21.5 mg NaClO/L.

281 The theoretical amount of 14% NaClO solution necessary for iron and manganese stoichiometric
282 oxidation was calculated for comparison. This calculation was carried out under the worst conditions,
283 that is the presence of peak concentration values of the two metals and complete inefficiency of the air
284 sparging for iron oxidation.

285 The stoichiometric reactions for Fe and Mn oxidation through chlorine are shown in Eqs. 2 and 3

286



289

290 Consequently, the stoichiometric chlorine doses for the oxidation of iron and manganese were of 0.67
291 mg NaClO/mg Fe²⁺ and 1.36 mg NaClO/mg Mn²⁺, respectively.

292 The maximum concentrations of iron and manganese found in the last five years in the groundwater
293 collected from well n.2 (the one with the lowest quality) were of 4167 µg/L for iron (detected in April
294 2016) and 774 µg/L for manganese (detected in April 2017). As it can be seen from Table 4, in the
295 presence of peak concentrations, a dose of 27.46 mg/L of 14% NaClO solution was necessary for the

296 oxidation of the two metals. Consequently, the theoretical amount of 14% NaClO solution to be used for
 297 the oxidation of iron and manganese, from June 2017 to March 2018, was calculated to be equal to 2680
 298 kg. The calculated amount, even under the worst conditions, was only approx. 18% of the amount actually
 299 purchased and used in the WTP. At a first glance it seemed that the oxidant was indeed overdosed, with
 300 a consequent overexploit of the GAC filter and a need of extra amounts of the chlorine suppressor agent.

301

302 Table 4. Theoretical chlorine doses for the oxidation of peak concentrations of iron and manganese

Species	MW (g/mol)	Peak concentration ($\mu\text{g/L}$)	NaClO dose ($\mu\text{g/L}$)	14% NaClO solution dose (mg/L)
Fe^{2+}	55.845	4167	2791.9	
Mn^{2+}	54.938	774	1052.6	
Total			3844.5	27.46

303

304 An overdose of NaClO could have several negative effects on the plant. The oxidant that was not
 305 consumed for the oxidation of species in a reduced form has to be suppressed, to avoid that it comes in
 306 contact with the membranes of microfiltration and RO. In fact, the final sections of the plant (i.e.
 307 microfiltration and RO) cannot tolerate concentrations of free chlorine of more than 0.1 mg/L. The GAC
 308 column is used for this precise purpose, but if the concentrations of residual free chlorine are too high,
 309 due to an overdose of NaClO solution, the GAC is not sufficient and the low concentrations required by
 310 the membranes can only be achieved by using chlorine suppressor substances, thus determining
 311 additional costs for the plant.

312 The second critical issue concerned the process of backwashing of the dual media (quartzite and
 313 pyrolusite) filter. At present, the filter is subjected to a backwashing process made of three subsequent
 314 phases: with air, with the RO concentrate (countercurrent) and, finally, with the water from the third

315 compartment (co-current) of the aeration – settling chamber. All the exhaust water from both the second
316 and the third phase of the backwashing is sent to the winery’s WWTP.

317 After the identification of the above mentioned two critical issues, some solutions were studied with the
318 aim of improving the management of the WTP and reducing the operating costs of the water treatment
319 process.

320

321 **3.2 Solutions to optimize the water treatment process**

322 **3.2.1 NaClO dosage for iron and manganese oxidation**

323 In Section 3.1 it was observed that the amount of the 14% NaClO solution actually purchased and used
324 for the process of oxidation of Fe and Mn in the WTP was at least five times more than the amount
325 calculated basing on stoichiometric considerations. The oxidant dose found with the theoretical approach
326 was subsequently verified with the aid of pilot tests carried out with real water samples collected at the
327 inlet of the WTP. The real need of NaClO for iron oxidation had to be demonstrated, because the air
328 distributed in the first of the three-compartment chamber was used exactly with the aim of facilitating
329 the iron oxidation process.

330 The tests described in Section 2.4 were used to quantify the right amount of NaClO solution necessary
331 to obtain the oxidation and consequent removal of iron and manganese. The average values of the
332 parameters (ORP, Fe, Mn, free chlorine) of the water samples subjected to the tests described in Section
333 2.4 are listed in Table 5.

334 Table 5. Values of the parameters (ORP, Fe, Mn, free chlorine) of the water sample subjected to the pilot
 335 tests

	iron (mg/L)	manganese (mg/L)	ORP (mV)	free Cl (mg/L)	total Cl (mg/L)
Initial concentrations	2	0.2	-20	< DL	< DL
After 50 min aeration	< DL	0.2	120	< DL	< DL
NaClO 14% - 4 mg/L	< DL	0.2	230	< DL	< DL
NaClO 14% - 10 mg/L	< DL	0.2	350	< DL	< DL
NaClO 14% - 40 mg/L	< DL	< DL	520	0.3	0.5
End of the 3-compartment chamber	< DL	< DL	>700	> 1.5	> 1.5

336 DL, detection limit

337

338 It can be seen that the initial concentrations of iron and manganese were in the order of 2 mg/L and 0.2
 339 mg/L, respectively. The ORP of the raw water was negative, of -20 mV, in line with the values normally
 340 found in a groundwater. As expected, no free chlorine was detected. After the 50-minute aeration process
 341 the value of ORP increased to +120 mV. The aeration process determined an almost complete removal
 342 of iron; in fact, the residual concentration of dissolved iron decreased under the detection limit (0.05
 343 mg/L). This result demonstrated that the process of air sparging was sufficient for the oxidation of iron
 344 and that the NaClO was not necessary for that operation. Conversely, the concentration of manganese
 345 was not altered by the aeration.

346 As described in Section 2.4, after the step of aeration, the water sample was mixed with a dose of 4 mg/L
 347 (0.56 mg NaClO/L) of the 14% NaClO solution. After a 30-min contact, it was verified that the
 348 concentration of manganese was still unaltered. Only when the concentration of the 14% NaClO solution
 349 was increased up to 40 mg/L, the concentration of soluble manganese was reduced to values under the
 350 detection limit (0.05 mg/L). The results found in the tests were coherent with observations from the

351 literature. In fact, several lab, pilot and field tests, carried out since the 1960-s, have demonstrated that
352 the oxidation of iron with oxygen is relatively straightforward in low-TOC, low-mineral content
353 groundwaters [21-22]. Conversely, aeration has been found to be slow and ineffective, even at high pH
354 values, for Mn(II) oxidation. Furthermore, even the reaction between chlorine (HOCl, the hydrolysis
355 product of both gaseous Cl₂ and NaClO) and Mn(II) was too slow to be useful for water treatment, unless
356 the pH was raised to values above 9. The combination of the processes of adsorption and oxidation is
357 necessary to achieve high efficiencies in Mn(II) removal. When chlorinated water is passed through a
358 filter containing a medium coated with MnO₂, the removal will occur by adsorption to the granular
359 medium, and the adsorbed Mn(II) will gradually be oxidized to MnO₂ on the filter medium surface [23].
360 The results of the field tests demonstrated that the present amount of NaClO used for water treatment
361 was indeed overdosed. The present concentration of pure oxidant, 21.5 mg NaClO/L, could be reduced
362 by at least 75%, that is, lowered to 5.6 mg/L (or 40 mg/L of 14% NaClO solution), without altering the
363 capacity of the WTP of removing iron and manganese. Furthermore, the field tests demonstrated that an
364 efficient removal of iron could already be obtained with the sole aeration process. For this reason, in
365 order to indeed save chlorine, the introduction of the NaClO solution into water had to be moved
366 downstream the aeration chamber, so as to achieve the oxidation of iron effectively by using air.
367 It has to be underlined that the NaClO dose found in the test was in any case overestimated, because it
368 did not take into account of the combined effect of pyrolusite adsorption and chlorine oxidation in
369 manganese removal. The reduced utilization of the NaClO would not have only a direct effect on the cost
370 of the water treatment (see Section 3.3), but it also had indirect effects on a better utilization of the GAC
371 column and on the saving of chlorine suppressor substances.

372 **3.2.2 Backwashing of the dual media filter**

373 The analysis of the backwashing phases' sequence, the quality of the waters used for the process and the
374 availability of water flows of several natures in the WTP suggested that changes to improve the efficiency
375 of the backwashing process were possible. At present, after an initial air washing, the filter is backwashed
376 firstly with the RO concentrate and, subsequently, with the water coming from the third compartment of
377 the aeration – settling chamber.

378 However, according to the technical literature, the conventional sequence of the phases in a backwashing
379 process is a first water wash, followed by an air wash and a final second water wash of the filter media
380 [10, 24]. The first water wash aims to mainly dislodge the coarser solids accumulated in the filter media
381 pores. Practical experience had demonstrated that backwashing of filter media grains smaller than 0.8
382 mm with water only is difficult [25]. Therefore, a typical backwash cycle should include a
383 combination/sequence of air and water washing of the filtration media, where the air wash is used to
384 create greater turbulence and enhances particle scrubbing allowing to also dislodge the finer solids and
385 some of the bacterial film accumulated on the grains of the filtration media. Finally, the air wash is
386 followed by another water wash, which aims to remove the solids and air accumulated in the media and
387 to prepare the filtration bed for another filtration cycle [25].

388 In the context of the winery's WTP, starting the backwashing sequence with a water washing was
389 recommended, because of the accumulation of fine particles of iron oxides into the porosity of the filter
390 media. However, the utilization of the RO concentrate for the first water washing phase should be
391 avoided. In fact, on the one hand, the use of the RO concentrate, instead of a filtered effluent, for the
392 backwashing of the filter, has the positive effect of reducing the backwash volume and the energy needed
393 to pump extra groundwater to the WTP. On the other hand, because of the corrosive nature of the RO
394 concentrate, due to the high concentrations of alkali-earth metals and chlorides into the raw water,
395 backwashing with the RO concentrate is definitely not recommended [25].

396 The combination of the backwashing phases and water flows shown in Figure 3 allowed to increase the
397 efficiency of the backwashing process. As in Figure 3, the water from the third compartment of the
398 aeration settling chamber is used for the second co-current water washing phase. After being used for
399 backwashing, this water is stored in a tank and used for the first countercurrent backwashing operation.
400 Only after that, it is definitely sent to the WWTP. This scheme allowed to avoid the use of the RO
401 concentrate and to minimize the use of pre-treated water (after the preliminary aeration and settling
402 treatment) for the backwashing process.

403
404 **3.3 Impact of the process improvements on the water treatment costs**

405 The volume of the raw water collected from the wells during the survey's period, that is from June 2017
406 to March 2018, was of 89,260 m³ and the volume of finished water, that is at the outlet of the WTP and
407 ready for use, was of approx. 56,500 m³.

408 The survey campaign on the WTP, carried out as described in Section 2.3, and the analysis of costs,
409 carried out as described in Section 2.5, returned the costs for water treatment detailed in Table 6.

410 Table 6. Detail of the cost items for the water treatment in the winery's WTP under the old and the new
 411 scenario (i.e. with the introduction of the proposed solutions)

		old	new	
Operating costs	Amortization installments	5600 €	4480 € (-20%)	
	Maintenance	31230 €	25000 € (-20%)	
	Consulting	4000 €	4000 €	
	Non amortizable raw materials and consumables	11300 €	9050 (-20%)	
Chemicals	Antiscalant/anticorrosion (NapolyPO ₄ , 25-40%)	9660 €	9660 €	
	Antiscalant/anticorrosion (NaHEDP, < 5%)	3600 €	3600 €	
	Chlorine suppressor (NaHSO ₃)	6390 €	1600 (-75%)	
	14% NaClO solution	3675 €	920 (-75%)	
Energy costs (Unit cost of electrical energy 0.145 €/kWh)		Energy consumption (kWh)		
	Wells	19,300	2800 €	2800 €
	Pump stations	50,000	7240 €	7240 €
	Reverse osmosis	71,400	10350 €	10350 €
	Filter backwashing	1,730	250 €	250 €

412

413 The overall cost for water treatment from June 2017 to March 2018 (10 months) was of approx. 96.1 k€,
 414 of which 54.2% were for operating costs, 24.3% were for chemicals and 21.4% for energy, as detailed in
 415 Figure 4. Considering the same period, the consequent unit cost for water treatment was of 1.70 €/m³.
 416 This cost was approx. one half of the purchase cost of water for industrial purposes, equal to 4 €/m³, that
 417 can be supplied by a local company for energy and water distribution [26].

418 The solutions for a better management of the WTP presented in Section 3.2 had inevitably positive
 419 impacts on the reduction of water treatment costs. First of all, as shown in Figure 5, the reduced dose of
 420 oxidant had a direct impact on the saving of the NaClO solution and the chlorine suppressor agent. From
 421 the results of the field tests (see Section 3.1.2), it could be estimated that the chlorine consumption could
 422 be reduced by 75% without altering the efficiency in iron and manganese oxidation. Because of the lower

423 employed dose of chlorine, also the amount of chlorine suppressor could be reduced by at least 75%. The
424 reduced dose of oxidant had also a positive impact on the lifetime of the GAC column and, consequently,
425 on the aliquot of the amortization installment laid aside for the purchase of new GAC. That saving could
426 be estimated in the order of 20% of the original amortization installment. Over long times, the cautious
427 use of reagents had a certain positive impact on the costs for maintenance and for the purchase of
428 frequently used (i.e. non amortizable) consumables [27-28]. This saving was estimated in a further 20%.
429 The overall cost for water treatment, on a period of ten months, would then reduce from 96.1 k€ to 79.0
430 k€. Consequently, the unit cost for water treatment would lower from 1.70 €/m³ to 1.40 €/m³, with a
431 saving of approx. 20%. Furthermore, the reduced utilization of chemicals will make the WTP able to
432 produce the same volumes of water with the same quality but with a higher environmental sustainability.
433 Finally, it had to be considered that the quality of the groundwater used to satisfy the winery requirements
434 was not homogeneous. Water collected from wells n.1 and n.3 had a better quality than that collected
435 from well n.2. Field tests will have to be carried out to verify if the productivity of wells n.1 and n.3
436 could be increased, without affecting the characteristics of the groundwater, so as to definitely avoid the
437 utilization of well n.2. That intervention would make possible to further reduce the use of chemicals for
438 the groundwater treatment.

439

440 **4. Conclusions**

441 The treatment processes performed in the WTP owned by the winery were deemed to be adequate to
442 make the groundwater usable for cleaning operations. However, a survey carried out by the authors
443 revealed the presence of two critical issues in the WTP's management, concerning the Fe(II) and Mn(II)
444 oxidation and removal, and the backwashing of the dual media filter, respectively.

445 For what concerns Fe(II) and Mn(II) oxidation and removal, the results of pilot tests demonstrated that:

- 446 • the sole process of air sparging was sufficient for the oxidation of iron and the injection of the
447 14% NaClO solution was not necessary for that operation;
- 448 • the amount of NaClO returned by the survey and presently used for the water treatment was
449 indeed overdosed. The consequent concentration of pure oxidant, 21.5 mg NaClO/L, could be
450 reduced by at least 75%, that is, lowered to 5.6 mg/L (or 40 mg/L of 14% NaClO solution),
451 without altering the capacity of the WTP of removing iron and manganese;
- 452 • because an efficient removal of iron could be obtained already with the sole aeration process, in
453 order to indeed save chlorine, the introduction of the NaClO solution into water had to be moved
454 downstream the aeration chamber, so as to achieve the oxidation of iron effectively by using air.

455 With reference to the second critical issue, a new combination of water fluxes could improve the
456 efficiency of the dual media filter backwashing. The new backwashing scheme should include a first
457 countercurrent backwashing process with the water coming from the second backwashing step, and a
458 second co-current washing phase with the water from the third compartment of the aeration settling
459 chamber. This new fluxes' combination allowed to simultaneously avoid the use of the RO corrosive
460 concentrate and to minimize the use of high quality water.

461 The introduction of these solutions into the WTP had an undeniable positive impact on the final unit cost
462 of the treated water, that decreased from 1.70 €/m³ to 1.40 €/m³. Meanwhile, the reduced utilization of
463 chemicals will make the WTP able to produce water with the same quality but in a more environmentally
464 friendly way.

465

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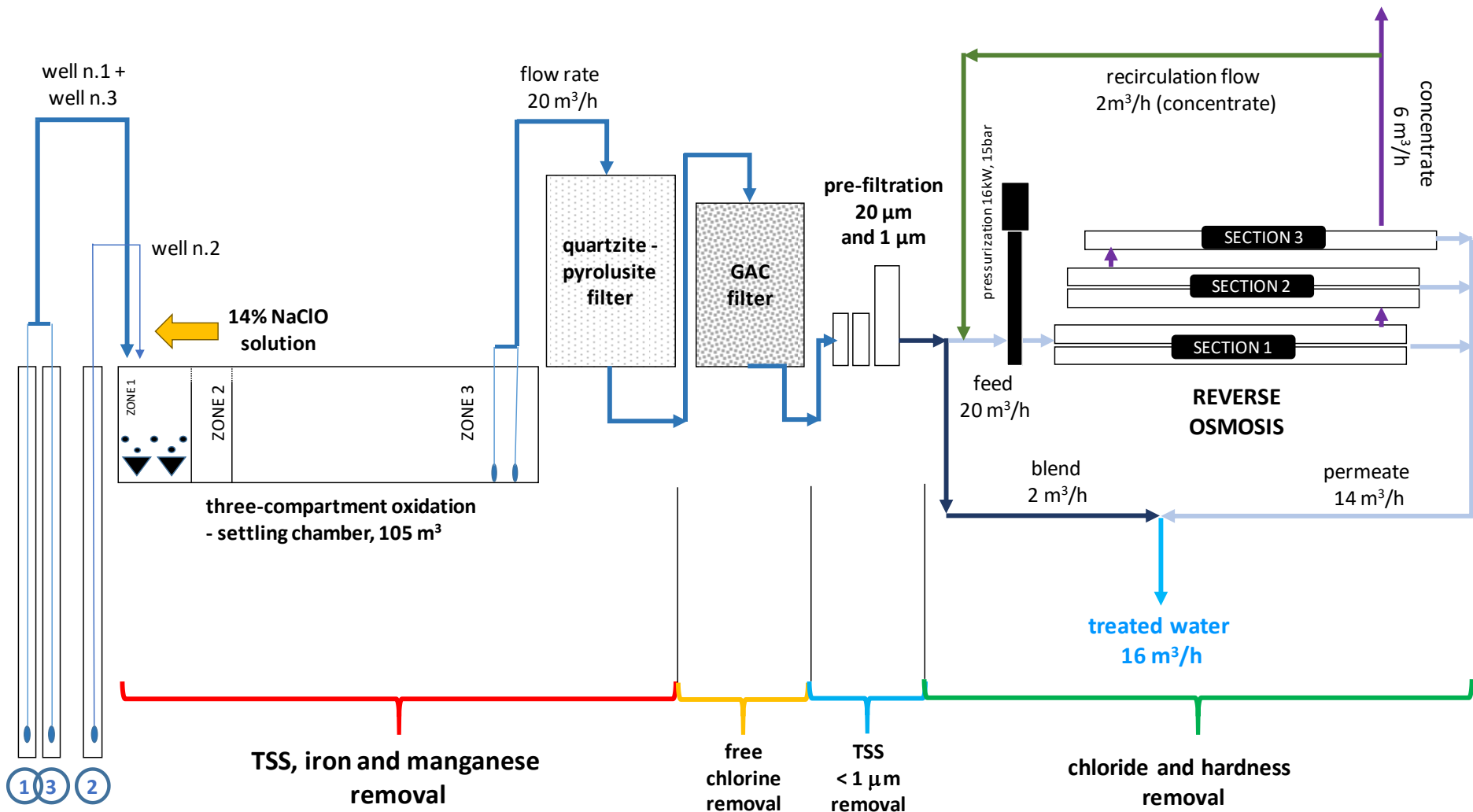


Figure 1. Scheme of the WTP



Figure 2. Apparatus for the aeration test (a) and for the rapid analysis of iron (b)

Optimization of the backwashing of the dual media filter

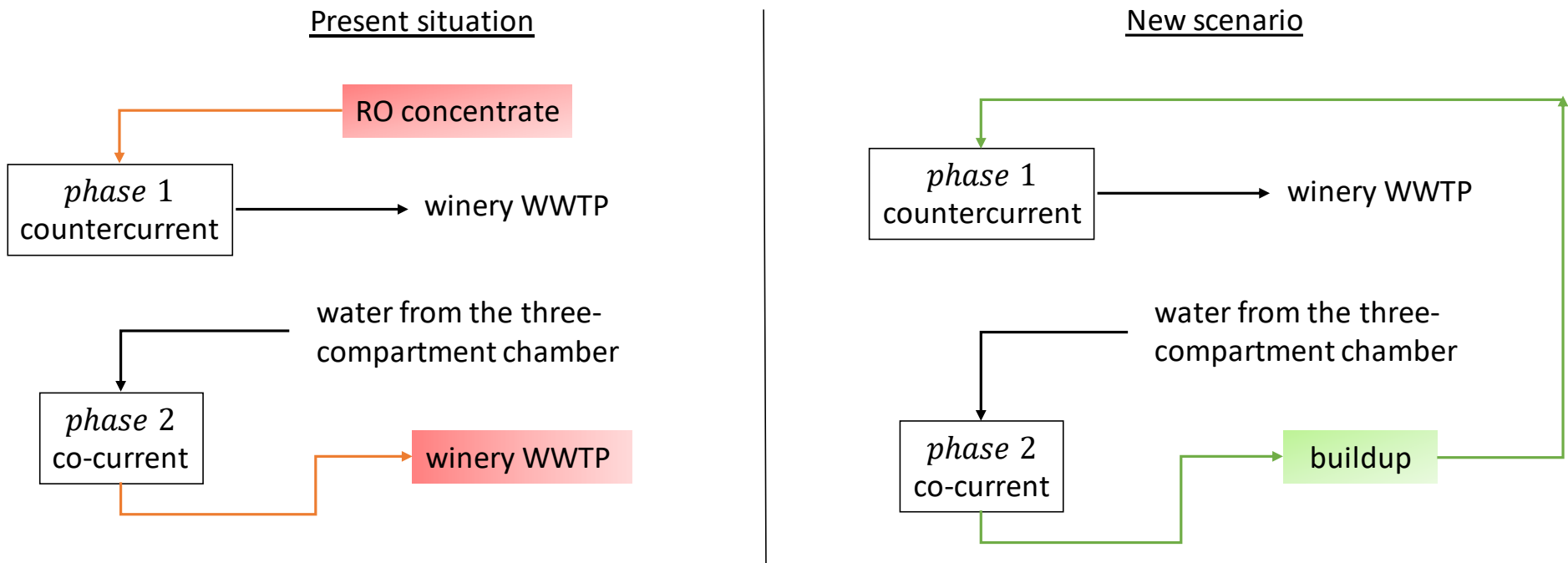


Figure 3. Combination of the backwashing phases and water flows in the present and in an optimized situation

PRESENT COSTS OF WATER TREATMENT

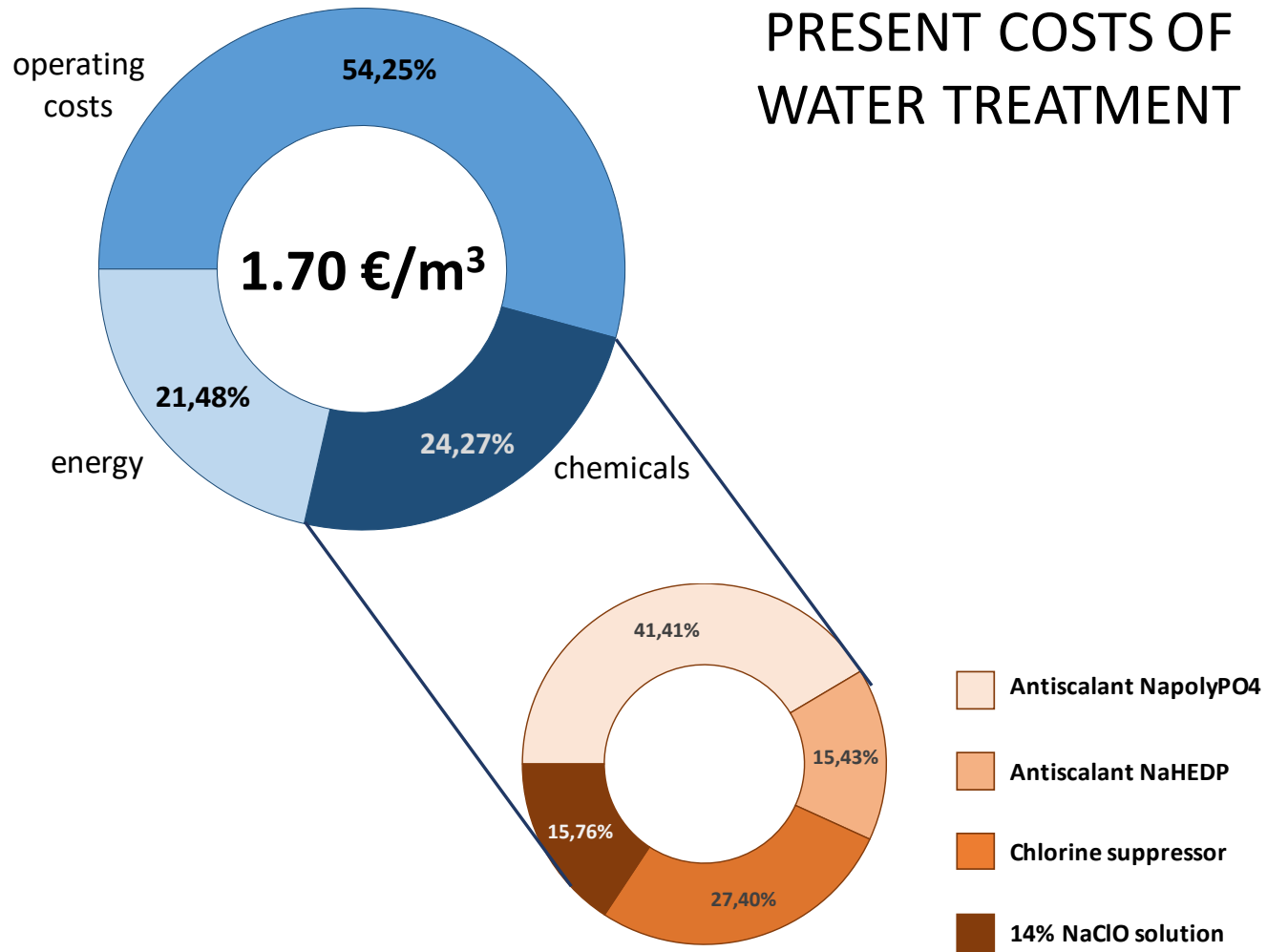


Figure 4. Detail of the water treatment costs in the present situation

COSTS OF WATER TREATMENT AFTER WTP OPTIMIZATION

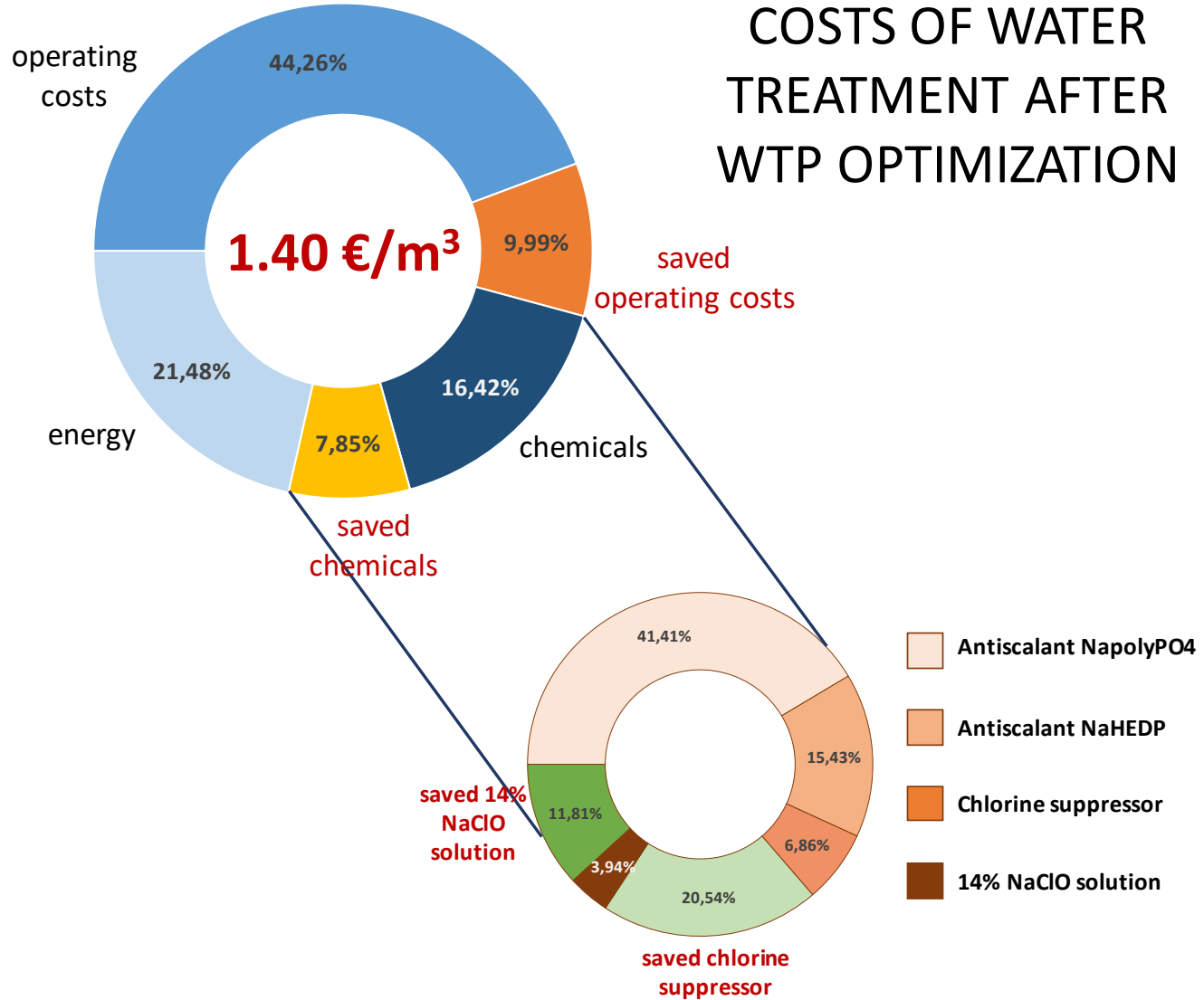


Figure 5. Detail of the water treatment costs in a future situation, after the WTP optimization

Table 2. Results of the analyses carried out on the groundwater collected from wells n.1 and n.3, and from well n.2, in the period 2015 – 2017

Parameter	Threshold value D.Lgs. 31/01	well n.1 + well n.3						well n.2					
		21/04/15	26/10/15	01/04/16	13/12/16	04/04/17	10/10/17	21/04/15	26/10/15	01/04/16	13/12/16	04/04/17	10/10/17
pH	6.5 – 9.5	6.8	6.6	6.7	7.0	6.8	7.0	6.7	6.5	6.7	7.0	6.7	6.8
Electrical conductivity ($\mu\text{S}/\text{cm}$ at 20°C)	2500	1299	1312	1370	1311	1317	1304	1431	1399	1494	1478	1512	1520
Chloride, Cl^- (mg/L)	250	172	197	198	208	196	184	178	187	197	231	228	221
Sulfate, SO_4^- (mg/L)	250	95.9	74	68,3	65,9	71,2	141	145	128	139	152	143	118
Calcium, Ca (mg/L)	-	171	169	155	147	147	152	214	212	184	150	152	158
Magnesium, Mg (mg/L)	-	26.5	24.8	27.5	28.4	27.5	46.7	26.2	24.1	18.7	55.9	54.4	67.3
Total hardness (°F)	15 - 50 (*)	53.6	52.4	50.0	45.7	48.0	57.2	64.4	62.8	53.6	60.4	60.4	67.2
Nitrate, NO_3^- (mg/L)	50	4.2	<1	1.3	5.2	4.3	<1	7.8	<1	<1	3.6	<1	<1
Nitrite, NO_2^- (mg/L)	0.5	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Ammonium, NH_4^+ (mg/L)	0.5	0.08	0.04	0.21	0.37	0.08	<0.05	0.11	0.10	0.32	0.45	0.14	<0.05
Iron, Fe ($\mu\text{g}/\text{L}$)	200	118	354	929	709	927	765	452	3688	4167	4155	4101	3272
Manganese, Mn ($\mu\text{g}/\text{L}$)	50	291	282	320	325	411	305	500	548	625	664	774	557
Arsenic, As ($\mu\text{g}/\text{L}$)	10	0.2	<0.1	<0.1	<0.1	<0.1	<0.1	0.4	0.4	<0.1	<0.1	<0.1	<0.1
Cadmium, Cd ($\mu\text{g}/\text{L}$)	5	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1
Chromium, Cr tot ($\mu\text{g}/\text{L}$)	50	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1
Mercury, Hg ($\mu\text{g}/\text{L}$)	1	<0.2	0.3	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2
Nichel, Ni ($\mu\text{g}/\text{L}$)	20	9.9	8.6	5.0	6.5	5.7	5.3	2.9	3.7	1.6	2.7	1.5	2.0
Lead, Pb ($\mu\text{g}/\text{L}$)	10	<1	<1	<1	<1	<1	<1	<1	<1	<1	1,6	<1	<1
Copper, Cu ($\mu\text{g}/\text{L}$)	1000	<1	<1	<1	<1	<1	<1	<1	2	<1	<1	<1	<1
Selenium, Se ($\mu\text{g}/\text{L}$)	10	<1	<1	<1	<1	<1	<1	1,2	1,2	<1	<1	<1	<1
Escherichia Coli (CFU/100 ml)	0	0	0	0	0	0	0	0	0	0	0	0	0
Total Coliforms (CFU/100 ml)	0	0	20	0	0	0	0	0	13	0	0	0	0

(*) recommended values