

## Electronic Supplementary Information

### Evidence for the natural origins of anomalously high chromium levels in soils of the Cecina Valley (Italy)

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**Table ESI-1** Georeferenced sampling points and corresponding concentration of Cr, Cu, Ni, Pb, Zn (mg kg<sup>-1</sup>) from Marina di Bibbona-Bolgheri (MBB), Cecina (CC) and Collemezzano (CM) areas. Values in bold exceed the threshold of contaminant concentration for residential soil use established by the Italian legislation (Legislative Decree 152/2006<sup>8</sup>).

Area/Sample names	longitude	latitude	Cr	Cu	Ni	Pb	Zn	
<b>MBB</b>	1	10.535810	43.237084	<b>193</b>	40	<b>206</b>	40	110
	2	10.538535	43.240136	<b>299</b>	33	<b>218</b>	40	87
	3	10.540174	43.239177	<b>305</b>	28	<b>213</b>	45	86
	4	10.542464	43.239146	<b>291</b>	37	<b>208</b>	53	99
	5	10.545954	43.240792	<b>296</b>	40	<b>190</b>	43	81
	6	10.544843	43.238754	<b>168</b>	40	<b>196</b>	55	98
	7	10.545603	43.241067	<b>203</b>	37	<b>210</b>	57	57
	8	10.563105	43.236714	<b>431</b>	49	<b>349</b>	46	81
	9	10.562922	43.234880	<b>494</b>	60	<b>369</b>	47	80
	10	10.563234	43.233597	<b>381</b>	55	<b>306</b>	41	81
	11	10.563754	43.231294	<b>323</b>	51	<b>329</b>	49	83
	12	10.570627	43.237106	<b>596</b>	57	<b>418</b>	48	87
	13	10.564986	43.236607	<b>420</b>	66	<b>341</b>	53	99
	14	10.561545	43.236420	<b>530</b>	45	<b>303</b>	52	88
	1 bis	10.542517	43.248105	<b>217</b>	29	<b>201</b>	46	86
	2 bis	10.555236	43.232409	<b>261</b>	44	<b>372</b>	46	88
	3 bis	10.562696	43.209617	<b>325</b>	42	<b>347</b>	37	70
	4 bis	10.564769	43.199719	<b>307</b>	35	<b>213</b>	44	83
	5 bis	10.550689	43.193896	<b>218</b>	49	<b>159</b>	50	92
	6 bis	10.575203	43.194804	<b>222</b>	57	<b>195</b>	61	95
	7 bis	10.590567	43.211574	151	18	94	43	48
	8 bis	10.570298	43.215158	<b>174</b>	63	<b>213</b>	47	62
	9 bis	10.566279	43.217834	<b>217</b>	66	<b>363</b>	49	69
	10 bis	10.571512	43.227442	<b>385</b>	45	<b>613</b>	<b>155</b>	29
	11 bis	10.602841	43.232247	<b>249</b>	103	<b>785</b>	63	57
	12 bis	10.579796	43.238277	<b>542</b>	76	<b>1190</b>	66	113
	13 bis	10.566218	43.245766	<b>298</b>	48	<b>328</b>	80	111
	14 bis	10.564370	43.250537	<b>331</b>	52	<b>804</b>	89	137
	scas1	10.541719	43.215943	<b>289</b>	17	<b>324</b>	22	55
	scas2	10.552672	43.218721	<b>236</b>	36	<b>294</b>	24	54
	scas3	10.549944	43.223297	<b>257</b>	39	<b>298</b>	26	63
	scas4	10.543571	43.228875	145	46	<b>285</b>	31	92
	scas5	10.585397	43.232499	<b>336</b>	41	<b>347</b>	34	63
	scas6	10.589731	43.223471	<b>272</b>	27	<b>169</b>	23	43
	scas7	10.559942	43.227627	<b>275</b>	33	<b>285</b>	33	64
	scas8	10.563087	43.230231	<b>212</b>	19	<b>255</b>	19	37
	scas9	10.544248	43.223986	<b>207</b>	47	<b>300</b>	25	89
	scas10	10.526842	43.236979	<b>162</b>	11	<b>279</b>	25	44
	scas11	10.546426	43.237058	<b>178</b>	51	<b>211</b>	34	87
	scas12	10.545361	43.234407	28	43	<b>273</b>	48	69
	scas13	10.556374	43.248061	<b>175</b>	34	<b>171</b>	32	74

scas14	10.563843	43.239108	<b>253</b>	39	<b>289</b>	33	63
scas15	10.579145	43.245039	<b>182</b>	27	<b>283</b>	29	49
scas16	10.573892	43.241474	<b>247</b>	29	<b>213</b>	27	46
scas17	10.583759	43.235800	<b>305</b>	42	<b>370</b>	29	60
scas18	10.590369	43.237581	<b>311</b>	43	<b>370</b>	26	59
scas19	10.597361	43.218592	<b>340</b>	38	<b>196</b>	22	53
scas20	10.576083	43.218482	<b>247</b>	32	<b>204</b>	18	49
scas21	10.580961	43.215723	<b>225</b>	28	<b>154</b>	21	46
scas22	10.614618	43.216549	80	38	77	24	52
scas23	10.617533	43.216922	104	14	81	20	35
scas24	10.614211	43.202535	<b>228</b>	32	69	32	49
scas25	10.662179	43.217534	<b>1070</b>	23	<b>1734</b>	19	32
scas26	10.581013	43.221512	<b>335</b>	33	<b>175</b>	23	49
scas27	10.569187	43.222719	<b>263</b>	45	<b>321</b>	28	63
scas28	10.562297	43.221976	<b>269</b>	32	<b>263</b>	28	51
scas29	10.552906	43.229857	<b>371</b>	44	<b>345</b>	38	78
scas30	10.569313	43.232937	<b>272</b>	48	<b>323</b>	40	81
scas31	10.569015	43.237164	<b>251</b>	48	<b>265</b>	39	59
scas32	10.568912	43.235554	<b>360</b>	48	<b>389</b>	40	55
scas33	10.564559	43.238684	<b>270</b>	47	<b>338</b>	48	74

**CC**

1	10.561654	43.236338	<b>255</b>	48	<b>515</b>	55	115
2	10.510432	43.300029	<b>189</b>	35	<b>232</b>	58	93
3	10.511031	43.298859	<b>211</b>	46	<b>329</b>	65	108
4	10.511702	43.297049	<b>200</b>	41	<b>256</b>	67	104
5	10.513548	43.293964	<b>230</b>	40	<b>227</b>	65	91
6	10.511842	43.293752	113	46	<b>248</b>	61	103
7	10.510736	43.293893	92	54	<b>257</b>	67	136
8	10.512301	43.295880	133	62	<b>281</b>	81	133
9	10.540885	43.303044	78	50	72	47	49
10	10.540869	43.302918	97	24	<b>146</b>	43	61
11	10.540213	43.303296	74	83	70	52	57
12	10.540016	43.303308	135	32	<b>125</b>	49	70
13	10.539374	43.303281	97	41	62	51	54
14	10.538515	43.303427	101	83	83	51	58
15	10.539122	43.303068	105	34	64	56	50
15 bis	10.502695	43.298744	135	56	<b>175</b>	47	107
16 bis	10.500851	43.302955	<b>152</b>	56	<b>229</b>	50	76
17 bis	10.511875	43.305052	<b>313</b>	39	<b>170</b>	40	67
18 bis	10.526944	43.300692	139	<b>145</b>	98	32	46
19 bis	10.527865	43.296619	<b>158</b>	107	67	37	46
20 bis	10.537249	43.298690	110	21	53	28	33
21 bis	10.539391	43.306891	<b>150</b>	117	59	28	51
22 bis	10.539045	43.309300	136	49	44	31	42
23 bis	10.535885	43.305714	<b>157</b>	<b>131</b>	66	36	52
scec1	10.541650	43.302097	96	29	64	39	45
scec2	10.536427	43.301312	76	22	52	33	37
scec4	10.534960	43.295920	106	32	78	38	44
scec5	10.530382	43.298665	87	19	51	37	39

scec6	10.531679	43.302699	113	50	91	38	41
scec7	10.528368	43.305877	135	25	93	37	46
scec8	10.523441	43.304106	94	37	<b>124</b>	46	55
scec9	10.510062	43.307003	<b>151</b>	34	<b>244</b>	50	65
scec10	10.516027	43.305897	99	33	89	40	50
scec11	10.508916	43.303533	149	29	<b>169</b>	44	59
scec12	10.512108	43.302501	<b>237</b>	26	<b>290</b>	41	62
scec13	10.517913	43.301920	145	26	77	40	45
scec14	10.516066	43.298045	<b>290</b>	22	117	36	53
scec15	10.520405	43.298024	129	27	67	36	38
scec16	10.514792	43.294388	<b>172</b>	40	<b>183</b>	44	57
scec17	10.506493	43.296290	92	34	<b>163</b>	48	79
101zuc	10.510584	43.308653	84	34	<b>120</b>	<b>519</b>	149
102zuc	10.509201	43.307095	<b>175</b>	45	<b>309</b>	<b>153</b>	<b>161</b>
103zuc	10.509796	43.308379	61	39	75	79	83
104zuc	10.506339	43.308051	37	35	54	93	99
105zuc	10.507752	43.308816	78	31	93	43	67
106zuc	10.508750	43.308290	66	51	106	<b>203</b>	73

<b>CM</b>	1	10.506260	43.335794	117	92	<b>170</b>	45	81
	2	10.509550	43.336120	140	52	<b>212</b>	52	69
	3	10.518441	43.337002	<b>180</b>	58	<b>243</b>	57	51
	4	10.522191	43.334539	<b>212</b>	28	<b>268</b>	34	46
	5	10.516206	43.341399	85	<b>157</b>	<b>126</b>	38	40
	6	10.503590	43.341547	69	33	66	34	34
	7	10.504287	43.347787	119	87	<b>173</b>	33	46
	8	10.509005	43.347995	96	46	111	36	52
	9	10.511157	43.348228	96	21	<b>144</b>	33	48
	10	10.512187	43.348943	<b>151</b>	28	<b>170</b>	34	50
	11	10.516509	43.349597	133	22	<b>246</b>	33	58
	12	10.516867	43.348620	<b>167</b>	31	<b>249</b>	33	70
	13	10.518102	43.349126	<b>188</b>	97	<b>210</b>	47	<b>176</b>
	14	10.519589	43.349422	106	21	<b>125</b>	37	37
	15	10.508631	43.340382	131	78	<b>153</b>	49	51
	16	10.527819	43.342019	<b>234</b>	24	<b>306</b>	35	60
	17	10.523825	43.350040	<b>185</b>	22	<b>235</b>	31	61
	18	10.527982	43.355415	93	119	<b>214</b>	27	43
	19	10.530671	43.360790	57	52	94	41	42
	20	10.527406	43.359987	67	57	117	34	32
	21	10.516861	43.356769	71	24	<b>125</b>	26	30
	22	10.510324	43.357405	93	25	<b>128</b>	43	33
	23	10.500870	43.350353	89	30	<b>152</b>	28	45
	24	10.483832	43.352430	98	27	100	39	53
	25	10.478518	43.355632	82	21	77	25	30
	26	10.484396	43.359365	88	47	80	30	36
	27	10.492969	43.360235	116	45	115	31	49
	28	10.500048	43.365059	78	26	75	30	33
	29	10.509497	43.367852	83	62	108	35	33
	30	10.497936	43.357982	92	49	118	28	39
	31	10.494874	43.355375	88	36	90	30	45

32	10.476523	43.360890	121	23	74	33	38
33	10.469711	43.369594	<b>154</b>	56	<b>136</b>	32	44
34	10.478855	43.365470	<b>174</b>	45	99	38	56
35	10.486838	43.365888	<b>164</b>	25	94	33	43
36	10.496315	43.368844	125	32	105	35	45
37	10.484490	43.375346	107	15	83	37	38
38	10.485924	43.372410	146	65	<b>223</b>	40	85
39	10.486157	43.378440	124	36	84	42	51
<b>Threshold limits (mg kg<sup>-1</sup>)</b>	<b>residential, public or private uses</b>		<b>150</b> <small>(tot)</small>	<b>120</b>	<b>120</b>	<b>100</b>	<b>150</b>
			<b>2</b> <small>(Cr VI)</small>	-	-	-	-
	<b>industrial or commercial uses</b>		<b>800</b> <small>(tot)</small>	<b>600</b>	<b>500</b>	<b>1000</b>	<b>1500</b>
			<b>15</b> <small>(Cr VI)</small>	-	-	-	-

**Figure ESI-1** Detailed fitting results (LCF) of XANES spectra from soil samples with model compounds.

