SUPPLEMENTARY INFORMATION 1

Quantification of free and cysteinylated aldehydes in samples derived from different stages of the industrial-scale malting process A

Compounds: 2MP = 2-methylpropanal, 2MB = 2-methylbutanal, 3MB = 3-methylbutanal, MET = methional, PHE = phenylacetaldehyde, FUR = furfural, HEX = hexanal, T2N = *trans*-2 nonenal, 2MP-CYS = cysteinylated 2-methylpropanal, 2MB-CYS = cysteinylated 2-methylbutanal, 3MB-CYS = cysteinylated 3-methylbutanal, MET-CYS = cysteinylated methional, PHE-CYS = cysteinylated phenylacetaldehyde, FUR-CYS = cysteinylated furfural (<LOD), and HEX-CYS = cysteinylated hexanal (cysteinylated *trans*-2-nonenal is not presented as the reference compound was not available).

Analysed samples: barley; GM = germinating barley (GM0 – onset of germination; GM1-GM4 = germinated for 1, 2, 3, 4 days, respectively); K = samples taken at kilning, after 12 up to 22h of kilning; C = samples taken at cooling, after 0 min to 50 min; FIN = finished malt (without rootlets). During kilning samples were collected from top, middle and bottom grain bed layer, while during cooling samples were taken from top layer.

Results are expressed as mean values (n=3) ± standard deviation. LOD = limit of detection; LOQ = limit of quantification.

Table S1.1. Quantification of free aldehydes in samples derived from different stages of the industrial-scale malting process A.

Free aldehydes (µg/kg dm)	**2MP**			**2MB**			**3MB**		
Raw material									
Barley	<LOD (35)			<LOD (30)			<LOD (136)		
Germination									
GM0	<LOD (35)			<LOD (30)			<LOD (136)		
GM1	<LOD (35)			<LOD (30)			<LOD (136)		
GM2	<LOQ (117)			<LOD (30)			<LOD (136)		
GM3	125 ± 22			<LOD (30)			<LOD (136)		
GM4	187 ± 24			<LOD (30)			<LOD (136)		
Kilning									
	Bottom	Middle	Top	Bottom	Middle	Top	Bottom	Middle	Top
K12.0	<LOQ (117)	<LOQ (117)	<LOD (35)	<LOD (30)	<LOD (30)	<LOD (30)	<LOQ (454)	<LOD (136)	<LOD (136)
K14.0	<LOQ (117)	<LOQ (117)	<LOD (35)	<LOD (30)	<LOD (30)	<LOD (30)	<LOQ (454)	<LOQ (454)	<LOD (136)
K16.0	142 ± 13	104 ± 16	<LOD (35)	<LOQ (99)	<LOQ (99)	<LOD (30)	<LOQ (454)	<LOQ (454)	<LOD (136)
K18.0	199 ± 5	163 ± 25	<LOD (35)	109 ± 9	<LOQ (99)	<LOD (30)	<LOQ (454)	<LOQ (454)	<LOD (136)
K18.5	183 ± 28	165 ± 26	<LOQ (117)	107 ± 22	<LOQ (99)	<LOD (30)	<LOQ (454)	<LOQ (454)	<LOD (136)
K19.0	236 ± 24	161 ± 21	<LOQ (117)	148 ± 35	<LOQ (99)	<LOQ (99)	<LOQ (454)	<LOQ (454)	<LOD (136)
K19.5	277 ± 33	252 ± 13	<LOQ (117)	173 ± 43	131 ± 13	<LOQ (99)	<LOQ (454)	<LOQ (454)	<LOD (136)
K20.0	352 ± 5	305 ± 10	<LOQ (117)	220 ± 19	207 ± 30	<LOQ (99)	<LOQ (454)	<LOQ (454)	<LOD (136)
K20.5	347 ± 37	326 ± 25	<LOQ (117)	244 ± 35	209 ± 28	<LOQ (99)	<LOQ (454)	<LOQ (454)	<LOQ (454)
K21.0	438 ± 1	333 ± 61	<LOQ (117)	296 ± 19	226 ± 21	<LOQ (99)	563 ± 34	<LOQ (454)	<LOQ (454)
K21.5	504 ± 58	-	<LOQ (117)	380 ± 49	-	<LOQ (99)	670 ± 78	-	<LOQ (454)
K22.0/C0	633 ± 48	570 ± 60	126 ± 12	520 ± 26	455 ± 19	131 ± 10	860 ± 37	783 ±23	<LOQ (454)
Cooling									
	Top			Top			Top		
C15	401 ± 28			300 ± 10			598 ± 29		
C30	417 ± 26			282 ± 45			549 ± 92		
C40	300 ± 36			273 ± 30			451 ± 72		
C50	354 ± 49			294 ± 13			527 ± 61		
Finished product									
Malt	375 ± 16			370 ± 25			655 ± 45		

Table S1.2. Quantification of free aldehydes in samples derived from different stages of the industrial-scale malting process A.

Free aldehydes (µg/kg dm)	**MET**			**PHE**			**FUR**		
Raw material									
Barley	<LOD (18)			<LOD (32)			<LOD (17)		
Germination									
GM0	<LOD (18)			<LOQ (107)			<LOD (17)		
GM1	<LOD (18)			<LOQ (107)			<LOD (17)		
GM2	<LOD (18)			<LOQ (107)			<LOD (17)		
GM3	<LOD (18)			<LOQ (107)			<LOD (17)		
GM4	<LOD (18)			<LOQ (107)			<LOD (17)		
Kilning									
	Bottom	Middle	Top	Bottom	Middle	Top	Bottom	Middle	Top
K12.0	<LOD (18)	<LOD (18)	<LOD (18)	<LOQ (107)	<LOQ (107)	<LOQ (107)	<LOD (17)	<LOD (17)	<LOD (17)
K14.0	<LOD (18)	<LOD (18)	<LOD (18)	<LOQ (107)	<LOQ (107)	<LOQ (107)	<LOD (17)	<LOD (17)	<LOD (17)
K16.0	<LOD (18)	<LOD (18)	<LOD (18)	112 ± 6	<LOQ (107)	<LOQ (107)	<LOD (17)	<LOD (17)	<LOD (17)
K18.0	<LOD (18)	<LOD (18)	<LOD (18)	161 ± 25	124 ± 15	<LOQ (107)	<LOD (17)	<LOD (17)	<LOD (17)
K18.5	<LOD (18)	<LOD (18)	<LOD (18)	134 ±15	108 ± 18	<LOQ (107)	<LOD (17)	<LOD (17)	<LOD (17)
K19.0	<LOD (18)	<LOD (18)	<LOD (18)	167 ± 28	112 ± 15	<LOQ (107)	58 ± 17	<LOD (17)	<LOD (17)
K19.5	<LOD (18)	<LOD (18)	<LOD (18)	171 ± 38	153 ± 22	<LOQ (107)	55 ± 23	58 ± 9	<LOD (17)
K20.0	<LOD (18)	<LOD (18)	<LOD (18)	256 ± 33	218 ± 36	<LOQ (107)	76 ± 18	75 ± 12	<LOQ (58)
K20.5	<LOD (18)	<LOD (18)	<LOD (18)	244 ± 39	240 ± 55	<LOQ (107)	83 ± 10	80 ± 15	<LOQ (58)
K21.0	<LOD (18)	<LOD (18)	<LOD (18)	338 ± 52	284 ± 38	<LOQ (107)	111 ± 24	86 ± 11	<LOQ (58)
K21.5	90 ± 12	<LOD (18)	<LOD (18)	370 ± 57	-	<LOQ (107)	106 ± 20	-	74 ± 18
K22.0/C0	108 ± 31	<LOD (18)	<LOD (18)	524 ± 81	508 ± 72	175 ± 68	182 ± 32	141 ± 26	87 ± 5
Cooling									
	Top			Top			Top		
C15	<LOQ (59)			303 ± 28			159 ± 22		
C30	<LOQ (59)			284 ± 59			152 ± 23		
C40	<LOQ (59)			200 ± 44			151 ± 14		
C50	<LOQ (59)			243 ± 67			156 ± 12		
Finished product									
Malt	71 ± 11			380 ± 39			176 ± 16		

Table S1.3. Quantification of free aldehydes in samples derived from different stages of the industrial-scale malting process A.

Free aldehydes (µg/kg dm)	**HEX**			**T2N**		
Raw material						
Barley	<LOD (47)			<LOD (37)		
Germination						
GM0	<LOD (47)			<LOD (37)		
GM1	<LOQ (157)			<LOD (37)		
GM2	<LOQ (157)			<LOQ (123)		
GM3	172 ± 26			<LOQ (123)		
GM4	337 ± 73			<LOQ (123)		
Kilning						
	Bottom	Middle	Top	Bottom	Middle	Top
K12.0	509 ± 74	570 ± 61	310 ± 50	<LOQ (123)	<LOQ (123)	<LOQ (123)
K14.0	587 ± 5	571 ± 26	345 ± 50	<LOQ (123)	<LOQ (123)	<LOQ (123)
K16.0	463 ± 60	575 ± 25	356 ± 51	<LOQ (123)	<LOQ (123)	<LOQ (123)
K18.0	278 ± 50	356 ± 28	385 ± 32	<LOQ (123)	<LOQ (123)	<LOQ (123)
K18.5	302 ± 42	317 ± 48	257 ± 31	<LOQ (123)	<LOQ (123)	<LOQ (123)
K19.0	541 ± 85	365 ± 68	224 ± 30	<LOQ (123)	<LOQ (123)	<LOQ (123)
K19.5	500 ± 74	535 ± 32	294 ± 43	<LOQ (123)	<LOQ (123)	<LOQ (123)
K20.0	481 ± 51	440 ± 101	367 ± 46	129 ± 15	<LOQ (123)	<LOQ (123)
K20.5	443 ± 69	434 ± 42	294 ± 47	137 ± 19	127 ± 16	<LOQ (123)
K21.0	465 ± 76	447 ± 53	228 ± 28	155 ± 25	126 ± 19	<LOQ (123)
K21.5	486 ± 62	-	253 ± 34	194 ± 21	126 ± 17	<LOQ (123)
K22.0/C0	301 ± 71	441 ± 56	245 ± 37	215 ± 27	165 ± 27	126 ± 34
Cooling						
	Top			Top		
C15	366 ± 43			178 ± 31		
C30	305 ± 43			161 ± 26		
C40	271 ± 37			141 ± 10		
C50	319 ± 80			136 ± 12		
Finished product						
Malt	191 ± 29			124 ± 15		

Table S1.4. Quantification of cysteinylated aldehydes in samples derived from different stages of the industrial-scale malting process A.

Cysteinylated aldehydes (µg/kg dm)	**2MP-CYS**			**2MB-CYS**			**3MB-CYS**		
Raw material									
Barley	<LOD (25)			<LOD (5)			<LOD (24)		
Germination									
GM0	<LOD (25)			<LOD (5)			<LOD (24)		
GM1	<LOD (25)			<LOD (5)			<LOD (24)		
GM2	<LOD (25)			<LOD (5)			<LOD (24)		
GM3	<LOD (25)			<LOD (5)			<LOD (24)		
GM4	<LOD (25)			<LOD (5)			<LOD (24)		
Kilning									
	Bottom	Middle	Top	Bottom	Middle	Top	Bottom	Middle	Top
K12.0	<LOQ (83)	<LOD (25)	<LOD (25)	<LOD (5)	<LOD (5)	<LOD (5)	<LOD (24)	<LOD (24)	<LOD (24)
K14.0	<LOQ (83)	<LOD (25)	<LOD (25)	<LOD (5)	<LOD (5)	<LOD (5)	<LOD (24)	<LOD (24)	<LOD (24)
K16.0	<LOQ (83)	<LOD (25)	<LOD (25)	<LOD (5)	<LOD (5)	<LOD (5)	<LOD (24)	<LOQ (48)	<LOD (24)
K18.0	<LOQ (83)	<LOD (25)	<LOD (25)	<LOQ (17)	<LOD (5)	<LOD (5)	<LOQ (48)	<LOQ (48)	<LOD (24)
K18.5	<LOQ (83)	<LOQ (83)	<LOD (25)	<LOQ (17)	<LOQ (17)	<LOD (5)	<LOQ (48)	<LOQ (48)	<LOD (24)
K19.0	<LOQ (83)	<LOQ (83)	<LOD (25)	<LOQ (17)	<LOQ (17)	<LOD (5)	<LOQ (48)	<LOQ (48)	<LOD (24)
K19.5	<LOQ (83)	<LOQ (83)	<LOD (25)	<LOQ (17)	<LOQ (17)	<LOD (5)	<LOQ (48)	<LOQ (48)	<LOD (24)
K20.0	<LOQ (83)	<LOQ (83)	<LOD (25)	<LOQ (17)	<LOQ (17)	<LOD (5)	52 ± 3	<LOQ (48)	<LOQ (48)
K20.5	<LOQ (83)	<LOQ (83)	<LOD (25)	19 ± 1	20 ± 2	<LOD (5)	68 ± 10	78 ± 2	<LOQ (48)
K21.0	<LOQ (83)	<LOQ (83)	<LOD (25)	20 ± 2	22 ± 4	<LOD (5)	74 ± 2	85 ± 9	<LOQ (48)
K21.5	<LOQ (83)	<LOQ (83)	<LOD (25)	29 ± 1	27 ± 3	<LOQ (17)	123 ± 12	93 ± 5	<LOQ (48)
K22.0/C0	<LOQ (83)	<LOQ (83)	<LOD (25)	38 ± 4	44 ± 3	<LOQ (17)	180 ± 6	202 ± 7	53 ± 3
Cooling									
	Top			Top			Top		
C15	111 ± 26			25 ± 1			109 ± 8		
C30	127 ± 9			23 ± 1			97 ± 5		
C40	153 ± 18			21 ± 2			89 ± 5		
C50	199 ± 30			20 ± 2			87 ± 5		
Finished product									
Malt	92 ± 6			36 ± 3			218 ± 20		

Table S1.5. Quantification of cysteinylated aldehydes in samples derived from different stages of the industrial-scale malting process A.

Cysteinylated aldehydes (µg/kg dm)	**MET-CYS**			**PHE-CYS**			**HEX-CYS**		
Raw material									
Barley	<LOD (7)			<LOD (11)			<LOD (14)		
Germination									
GM0	<LOD (7)			<LOD (11)			<LOD (14)		
GM1	<LOD (7)			<LOD (11)			<LOD (14)		
GM2	<LOD (7)			<LOD (11)			<LOQ (47)		
GM3	<LOD (7)			<LOD (11)			<LOQ (47)		
GM4	<LOD (7)			<LOD (11)			<LOQ (47)		
Kilning									
	Bottom	Middle	Top	Bottom	Middle	Top	Bottom	Middle	Top
K12.0	<LOD (7)	<LOD (7)	<LOD (7)	<LOD (11)	<LOD (11)	<LOD (11)	<LOD (14)	<LOD (14)	<LOQ (47)
K14.0	<LOD (7)	<LOD (7)	<LOD (7)	<LOD (11)	<LOD (11)	<LOD (11)	<LOD (14)	<LOD (14)	<LOQ (47)
K16.0	<LOD (7)	<LOD (7)	<LOD (7)	<LOD (11)	<LOQ (36)	<LOD (11)	<LOD (14)	<LOD (14)	<LOQ (47)
K18.0	<LOD (7)	<LOD (7)	<LOD (7)	<LOQ (36)	<LOQ (36)	<LOD (11)	<LOD (14)	<LOQ (47)	<LOQ (47)
K18.5	<LOD (7)	<LOD (7)	<LOD (7)	<LOQ (36)	<LOQ (36)	<LOD (11)	<LOD (14)	<LOQ (47)	<LOQ (47)
K19.0	<LOD (7)	<LOD (7)	<LOD (7)	<LOQ (36)	<LOQ (36)	<LOD (11)	<LOQ (47)	<LOQ (47)	<LOQ (47)
K19.5	<LOD (7)	<LOD (7)	<LOD (7)	37 ± 3	<LOQ (36)	<LOD (11)	<LOQ (47)	<LOQ (47)	<LOQ (47)
K20.0	<LOD (7)	<LOD (7)	<LOD (7)	45 ± 1	38 ± 3	<LOQ (36)	<LOQ (47)	<LOQ (47)	<LOQ (47)
K20.5	<LOQ (25)	<LOD (7)	<LOD (7)	50 ± 4	49 ± 4	<LOQ (36)	<LOQ (47)	<LOQ (47)	<LOQ (47)
K21.0	<LOQ (25)	<LOD (7)	<LOD (7)	64 ± 5	50 ± 2	<LOQ (36)	<LOQ (47)	<LOQ (47)	<LOQ (47)
K21.5	<LOQ (25)	<LOQ (25)	<LOD (7)	77 ± 6	71 ± 1	37 ± 2	<LOQ (47)	<LOQ (47)	<LOQ (47)
K22.0/C0	32 ± 2	<LOQ (25)	<LOD (7)	102 ± 2	101 ± 2	41 ± 2	<LOQ (47)	48 ± 1	<LOQ (47)
Cooling									
	Top			Top			Top		
C15	25 ± 1			63 ± 5			<LOQ (47)		
C30	21 ± 1			57 ± 3			<LOQ (47)		
C40	20 ± 2			58 ± 3			<LOQ (47)		
C50	22 ± 1			54 ± 2			<LOQ (47)		
Finished product									
Malt	27 ± 2			110 ± 7			65 ± 4		

SUPPLEMENTARY INFORMATION 2

Quantification of free and cysteinylated aldehydes in samples derived from different stages of the industrial-scale malting process B

Compounds: 2MP = 2-methylpropanal, 2MB = 2-methylbutanal, 3MB = 3-methylbutanal, MET = methional, PHE = phenylacetaldehyde, FUR = furfural, HEX = hexanal, T2N = *trans*-2 nonenal, 2MP-CYS = cysteinylated 2-methylpropanal, 2MB-CYS = cysteinylated 2-methylbutanal, 3MB-CYS = cysteinylated 3-methylbutanal, MET-CYS = cysteinylated methional, PHE-CYS = cysteinylated phenylacetaldehyde, FUR-CYS = cysteinylated furfural (<LOD), and HEX-CYS = cysteinylated hexanal (cysteinylated *trans*-2-nonenal is not presented as the reference compound was not available).

Analysed samples: barley; GM = germinating barley (GM0 – onset of germination; GM1-GM4 = germinated for 1, 2, 3, 4 days, respectively); K = samples taken at kilning, after 12 up to 22h of kilning; C = samples taken at cooling, after 0 min to 50 min; FIN = finished malt (without rootlets). During kilning samples were collected from top, middle and bottom grain bed layer, while during cooling samples were taken from top layer.

Results are expressed as mean values (n=3) ± standard deviation. LOD = limit of detection; LOQ = limit of quantification.

Table S2.1. Quantification of free aldehydes in samples derived from different stages of the industrial-scale malting process B.

Free aldehydes (μg/kg dm)	**2MP**			**2MB**			**3MB**		
Barley	<LOD (35)			<LOD (30)			<LOD (136)		
GM0	<LOD (35)			<LOD (30)			<LOD (136)		
GM1	<LOD (35)			<LOD (30)			<LOD (136)		
GM2	<LOQ (117)			<LOD (30)			<LOD (136)		
GM3	125 ± 16			<LOD (30)			<LOD (136)		
GM4	149 ± 16			<LOD (30)			<LOD (136)		
	Bottom	Middle	Top	Bottom	Middle	Top	Bottom	Middle	Top
K12.5	231 ± 15	<LOQ (117)	<LOQ (117)	152 ± 11	<LOD (30)	<LOD (30)	<LOQ (454)	<LOQ (454)	<LOD (136)
K13.0	261 ± 15	<LOQ (117)	<LOQ (117)	179 ± 12	<LOD (30)	<LOD (30)	490 ± 48	<LOQ (454)	<LOD (136)
K13.5	301 ± 33	<LOQ (117)	<LOQ (117)	218 ± 13	<LOD (30)	<LOD (30)	551 ± 51	<LOQ (454)	<LOD (136)
K14.0	383 ± 30	134 ± 28	<LOQ (117)	301 ± 39	<LOQ (99)	<LOD (30)	757 ± 40	<LOQ (454)	<LOD (136)
K14.5	389 ± 9	104 ± 24	<LOQ (117)	295 ± 18	<LOQ (99)	<LOD (30)	694 ± 116	<LOQ (454)	<LOD (136)
K15.0	591 ± 10	387 ± 14	<LOQ (117)	478 ± 34	323 ± 10	<LOD (30)	998 ± 51	798 ± 22	<LOD (136)
K15.5	609 ± 2	401 ± 17	<LOQ (117)	496 ± 40	327 ± 16	<LOD (30)	1,026 ± 78	803 ± 47	<LOD (136)
K16.0	689 ± 6	391 ± 46	<LOQ (117)	587 ± 48	328 ± 34	<LOD (30)	1,219 ± 106	805 ± 89	<LOD (136)
K16.5	704 ± 12	525 ± 87	<LOQ (117)	618 ± 40	478 ± 78	<LOD (30)	1,312 ± 104	1,083 ± 159	<LOD (136)
K17.0	834 ± 34	606 ± 97	<LOQ (117)	743 ± 44	388 ± 81	<LOD (30)	1,463 ± 84	1,113 ± 200	<LOD (136)
K17.5	780 ± 57	495 ± 63	<LOQ (117)	713 ± 42	431 ± 89	<LOD (30)	1,362 ± 72	914 ± 194	<LOD (136)
K18.0	877 ± 51	472 ± 41	<LOQ (117)	727 ± 189	401 ± 44	<LOD (30)	1,804 ± 96	889 ± 157	<LOD (136)
K18.5	1,034 ± 150	892 ± 43	<LOQ (117)	988 ± 225	810 ± 51	<LOQ (99)	2,214 ± 218	1,512 ± 112	<LOQ (454)
K19.0	1,248 ± 49	863 ± 32	196 ± 28	1,338 ± 107	840 ± 34	159 ± 12	2,748 ± 406	1,463 ± 48	<LOQ (454)
K19.5	1,367 ± 183	959 ± 56	257 ± 39	1,695 ± 274	875 ± 56	244 ± 41	3,288 ± 166	1,493 ± 67	490 ± 76
K20.0	1,455 ± 195	1,290 ± 56	298 ± 17	1,857 ± 124	1,324 ± 28	269 ± 22	3,835 ± 187	2,105 ± 33	549 ± 43
K21.5	1,572 ± 156	1,586 ± 131	349 ± 50	1,914 ± 307	1,634 ± 113	336 ± 43	4,147 ± 265	2,526 ± 125	663 ± 89
	Top			Top			Top		
C0	927 ± 114			858 ± 116			1,398 ± 155		
C10	690 ± 76			620 ± 110			1,049 ± 201		
C20	840 ± 73			743 ± 14			1,255 ± 36		
C30	1,002 ± 140			884 ± 144			1,437 ± 218		
C40	1,060 ± 160			1,036 ± 144			1,563 ± 266		
Malt	1,270 ± 234			1,252 ± 263			2,033 ± 138		

Table S2.2. Quantification of free aldehydes in samples derived from different stages of the industrial-scale malting process B.

Free aldehydes (µg/kg dm)	**MET**			**PHE**			**FUR**		
Barley	<LOD (18)			<LOD (32)			<LOD (17)		
GM0	<LOD (18)			<LOD (32)			<LOD (17)		
GM1	<LOD (18)			<LOD (32)			<LOD (17)		
GM2	<LOD (18)			<LOD (32)			<LOD (17)		
GM3	<LOD (18)			<LOD (32)			<LOD (17)		
GM4	<LOD (18)			<LOD (32)			<LOD (17)		
	Bottom	Middle	Top	Bottom	Middle	Top	Bottom	Middle	Top
K12.5	<LOD (18)	<LOD (18)	<LOD (18)	<LOQ (107)	<LOQ (107)	<LOD (32)	58 ± 12	<LOQ (58)	<LOD (17)
K13.0	<LOD (18)	<LOD (18)	<LOD (18)	<LOQ (107)	<LOQ (107)	<LOD (32)	97 ± 20	<LOQ (58)	<LOD (17)
K13.5	<LOD (18)	<LOD (18)	<LOD (18)	<LOQ (107)	<LOQ (107)	<LOD (32)	85 ± 8	<LOQ (58)	<LOD (17)
K14.0	<LOD (18)	<LOD (18)	<LOD (18)	347 ± 72	<LOQ (107)	<LOD (32)	141 ± 31	<LOQ (58)	<LOD (17)
K14.5	<LOD (18)	<LOD (18)	<LOD (18)	332 ± 48	<LOQ (107)	<LOD (32)	129 ± 16	<LOQ (58)	<LOD (17)
K15.0	<LOD (18)	<LOD (18)	<LOD (18)	412 ± 60	488 ± 11	<LOD (32)	188 ± 98	<LOQ (58)	<LOD (17)
K15.5	<LOD (18)	<LOD (18)	<LOD (18)	378 ± 71	466 ± 42	<LOD (32)	180 ± 101	<LOQ (58)	<LOD (17)
K16.0	<LOD (18)	<LOD (18)	<LOD (18)	459 ± 72	419 ± 41	<LOD (32)	218 ± 59	207 ± 23	<LOD (17)
K16.5	<LOD (18)	<LOD (18)	<LOD (18)	511 ± 63	522 ± 60	<LOD (32)	243 ± 87	205 ± 37	<LOQ (58)
K17.0	<LOD (18)	<LOD (18)	<LOD (18)	675 ± 35	640 ± 140	<LOD (32)	271 ± 53	149 ± 58	<LOQ (58)
K17.5	<LOD (18)	<LOD (18)	<LOD (18)	577 ± 40	446 ± 140	<LOD (32)	233 ± 53	139 ± 44	<LOQ (58)
K18.0	<LOD (18)	<LOD (18)	<LOD (18)	723 ± 54	448 ± 136	<LOD (32)	323 ± 68	162 ± 5	<LOQ (58)
K18.5	<LOQ (59)	<LOD (18)	<LOD (18)	974 ± 187	717 ± 138	<LOD (32)	468 ± 102	218 ± 36	<LOQ (58)
K19.0	<LOQ (59)	<LOQ (59)	<LOD (18)	1,276 ± 189	800 ± 159	<LOQ (107)	558 ± 117	271 ± 31	<LOQ (58)
K19.5	<LOQ (59)	<LOQ (59)	<LOD (18)	1,703 ± 82	919 ± 135	<LOQ (107)	755 ± 99	307 ± 28	<LOQ (58)
K20.0	<LOQ (59)	<LOQ (59)	<LOD (18)	1,788 ± 137	1,262 ± 74	315 ± 18	790 ± 58	416 ± 60	<LOQ (58)
K21.5	<LOQ (59)	<LOQ (59)	<LOD (18)	1,940 ± 43	1,690 ± 135	275 ± 41	914 ± 84	558 ± 50	<LOQ (58)
	Top			Top			Top		
C0	158 ± 46			847 ± 161			541 ± 25		
C10	75 ± 37			455 ± 144			286 ± 58		
C20	105 ± 32			638 ± 54			413 ± 55		
C30	125 ± 15			758 ± 85			434 ± 23		
C40	196 ± 46			1,086 ± 198			599 ± 82		
Malt	312 ± 46			1,493 ± 362			705 ± 135		

Table S2.3. Quantification of free aldehydes in samples derived from different stages of the industrial-scale malting process B.

Free aldehydes (μg/kg dm)	**HEX**			**T2N**		
Barley	<LOD (47)			<LOD (37)		
GM0	<LOD (47)			<LOD (37)		
GM1	<LOQ (157)			<LOD (37)		
GM2	<LOQ (157)			<LOQ (123)		
GM3	161 ± 31			<LOQ (123)		
GM4	215 ± 42			<LOQ (123)		
	Bottom	Middle	Top	Bottom	Middle	Top
K12.5	557 ± 59	462 ± 88	516 ± 116	<LOQ (123)	<LOQ (123)	<LOQ (123)
K13.0	642 ± 84	691 ± 168	461 ± 28	<LOQ (123)	<LOQ (123)	<LOQ (123)
K13.5	673 ± 112	648 ± 79	602 ± 43	<LOQ (123)	<LOQ (123)	<LOQ (123)
K14.0	752 ± 111	730 ± 160	397 ± 131	<LOQ (123)	<LOQ (123)	<LOQ (123)
K14.5	674 ± 91	659 ± 193	468 ± 105	<LOQ (123)	<LOQ (123)	<LOQ (123)
K15.0	531 ± 98	812 ± 101	518 ± 50	<LOQ (123)	<LOQ (123)	<LOQ (123)
K15.5	527 ± 101	731 ± 140	1,011 ± 107	<LOQ (123)	<LOQ (123)	<LOQ (123)
K16.0	496 ± 59	800 ± 94	961 ± 123	<LOQ (123)	<LOQ (123)	<LOQ (123)
K16.5	499 ± 87	884 ± 148	1,101 ± 85	<LOQ (123)	<LOQ (123)	<LOQ (123)
K17.0	494 ± 53	831 ± 149	789 ± 139	<LOQ (123)	<LOQ (123)	<LOQ (123)
K17.5	402 ± 53	572 ± 42	811 ± 99	<LOQ (123)	<LOQ (123)	<LOQ (123)
K18.0	488 ± 68	244 ± 42	636 ± 107	<LOQ (123)	<LOQ (123)	<LOQ (123)
K18.5	697 ± 102	243 ± 50	275 ± 69	109 ± 18	<LOQ (123)	<LOQ (123)
K19.0	808 ± 117	453 ± 66	371 ± 75	178 ± 42	126 ± 36	<LOQ (123)
K19.5	867 ± 99	403 ± 50	328 ± 137	234 ± 48	195 ± 41	151 ± 26
K20.0	634 ± 58	402 ± 70	348 ± 73	273 ± 44	245 ± 49	185 ± 20
K21.5	553 ± 84	400 ± 57	401 ± 26	326 ± 55	328 ± 44	196 ± 26
	Top			Top		
C0	257 ± 128			345 ± 46		
C10	265 ± 72			234 ± 19		
C20	274 ± 52			232 ± 29		
C30	159 ± 69			201 ± 19		
C40	396 ± 49			220 ± 16		
Malt	358 ± 42			244 ± 43		

Table S2.4. Quantification of cysteinylated aldehydes in samples derived from different stages of the industrial-scale malting process B.

Cysteinylated aldehydes (µg/kg dm)	**2MP-CYS**			**2MB-CYS**			**3MB-CYS**		
Barley	<LOD (25)			<LOD (5)			<LOD (24)		
GM0	<LOD (25)			<LOD (5)			<LOD (24)		
GM1	<LOD (25)			<LOD (5)			<LOD (24)		
GM2	<LOD (25)			<LOD (5)			<LOD (24)		
GM3	<LOD (25)			<LOD (5)			<LOD (24)		
GM4	<LOD (25)			<LOD (5)			<LOD (24)		
	Bottom	Middle	Top	Bottom	Middle	Top	Bottom	Middle	Top
K12.5	<LOD (25)	<LOD (25)	<LOD (25)	<LOD (5)	<LOD (5)	<LOD (5)	<LOQ (48)	<LOD (24)	<LOD (24)
K13.0	<LOD (25)	<LOD (25)	<LOD (25)	<LOD (5)	<LOD (5)	<LOD (5)	<LOQ (48)	<LOQ (48)	<LOD (24)
K13.5	<LOD (25)	<LOD (25)	<LOD (25)	68 ± 5	<LOD (5)	<LOD (5)	<LOQ (48)	<LOQ (48)	<LOD (24)
K14.0	<LOQ (83)	<LOD (25)	<LOD (25)	70 ± 6	<LOD (5)	<LOD (5)	56 ± 3	<LOQ (48)	<LOD (24)
K14.5	<LOQ (83)	<LOQ (83)	<LOD (25)	77 ± 5	<LOD (5)	<LOD (5)	66 ± 3	<LOQ (48)	<LOD (24)
K15.0	<LOQ (83)	<LOQ (83)	<LOD (25)	83 ± 8	<LOD (5)	<LOD (5)	101 ± 9	56 ± 5	<LOD (24)
K15.5	<LOQ (83)	<LOQ (83)	<LOD (25)	78 ± 6	<LOD (5)	<LOD (5)	126 ± 10	73 ± 6	<LOD (24)
K16.0	92 ± 7	<LOQ (83)	<LOD (25)	89 ± 4	<LOD (5)	<LOD (5)	153 ± 6	78 ± 3	<LOD (24)
K16.5	95 ± 1	<LOQ (83)	<LOD (25)	96 ± 6	<LOD (5)	<LOD (5)	176 ± 3	115 ± 5	<LOD (24)
K17.0	108 ± 4	103 ± 4	<LOD (25)	101 ± 4	<LOD (5)	<LOD (5)	187 ± 12	178 ± 6	<LOD (24)
K17.5	114 ± 6	150 ± 6	<LOD (25)	87 ± 1	<LOD (5)	<LOD (5)	203 ± 12	263 ± 7	<LOD (24)
K18.0	138 ± 2	140 ± 4	<LOD (25)	99 ± 4	50 ± 6	<LOD (5)	243 ± 30	283 ± 9	<LOD (24)
K18.5	182 ± 2	215 ± 7	<LOD (25)	135 ± 6	77 ± 5	<LOD (5)	370 ± 16	410 ± 13	<LOD (24)
K19.0	265 ± 13	220 ± 9	<LOD (25)	164 ± 4	93 ± 10	<LOD (5)	661 ± 18	512 ± 30	51 ± 4
K19.5	281 ± 9	295 ± 9	<LOQ (83)	181 ± 4	115 ± 7	<LOQ (17)	701 ± 15	707 ± 23	61 ± 9
K20.0	349 ± 6	333 ± 13	<LOQ (83)	211 ± 7	140 ± 12	<LOQ (17)	921 ± 5	839 ± 27	117 ± 3
K21.5	372 ± 4	420 ± 8	<LOQ (83)	219 ± 13	179 ± 19	26 ± 3	1,008 ± 27	916 ± 29	161 ± 2
	Top			Top			Top		
C0	274 ± 18			49 ± 1			208 ± 15		
C10	248 ± 6			29 ± 2			141 ± 6		
C20	282 ± 7			33 ± 1			159 ± 4		
C30	336 ± 20			42 ± 1			191 ± 12		
C40	354 ± 6			46 ± 2			222 ± 11		
Malt	334 ± 4			100 ± 1			477 ± 21		

Table S2.5. Quantification of cysteinylated aldehydes in samples derived from different stages of the industrial-scale malting process B.

Cysteinylated aldehydes (µg/kg dm)	**MET-CYS**			**PHE-CYS**			**HEX-CYS**		
Barley	<LOD (7)			<LOD (11)			<LOD (14)		
GM0	<LOD (7)			<LOD (11)			<LOD (14)		
GM1	<LOD (7)			<LOD (11)			<LOD (14)		
GM2	<LOD (7)			<LOD (11)			<LOD (14)		
GM3	<LOD (7)			<LOD (11)			<LOD (14)		
GM4	<LOD (7)			<LOD (11)			<LOD (14)		
	Bottom	Middle	Top	Bottom	Middle	Top	Bottom	Middle	Top
K12.5	<LOD (7)	<LOD (7)	<LOD (7)	39 ± 5	<LOD (11)	<LOD (11)	<LOQ (47)	<LOQ (47)	<LOD (14)
K13.0	<LOD (7)	<LOD (7)	<LOD (7)	36 ± 5	<LOQ (36)	<LOD (11)	<LOD (14)	61 ± 2	<LOD (14)
K13.5	<LOQ (25)	<LOQ (25)	<LOD (7)	43 ± 4	<LOQ (36)	<LOD (11)	<LOD (14)	67 ± 3	<LOD (14)
K14.0	<LOQ (25)	<LOQ (25)	<LOD (7)	56 ± 1	44 ± 1	<LOD (11)	<LOQ (47)	63 ± 4	<LOD (14)
K14.5	<LOQ (25)	<LOQ (25)	<LOD (7)	58 ± 3	51 ± 4	<LOD (11)	<LOQ (47)	79 ± 3	<LOD (14)
K15.0	<LOQ (25)	<LOQ (25)	<LOD (7)	77 ± 6	56 ± 2	<LOD (11)	<LOQ (47)	24 ± 1	<LOD (14)
K15.5	26 ± 4	±	<LOD (7)	92 ± 9	73 ± 3	<LOD (11)	<LOQ (47)	33 ± 1	<LOD (14)
K16.0	28 ± 5	±	<LOD (7)	104 ± 1	69 ± 3	<LOD (11)	<LOQ (47)	31 ± 1	<LOD (14)
K16.5	32 ± 2	±	<LOD (7)	102 ± 3	90 ± 7	<LOD (11)	<LOQ (47)	34 ± 2	<LOD (14)
K17.0	32 ± 5	±	<LOD (7)	123 ± 4	106 ± 2	<LOD (11)	<LOQ (47)	38 ± 2	<LOD (14)
K17.5	35 ± 2	±	<LOD (7)	120 ± 1	155 ± 5	<LOD (11)	<LOQ (47)	55 ± 4	<LOQ (47)
K18.0	40 ± 4	±	<LOD (7)	141 ± 5	172 ± 8	<LOD (11)	<LOQ (47)	52 ± 2	<LOQ (47)
K18.5	51 ± 5	±	<LOQ (25)	192 ± 13	207 ± 1	<LOQ (36)	<LOQ (47)	85 ± 3	<LOQ (47)
K19.0	73 ± 1	±	<LOQ (25)	249 ± 2	222 ± 13	50 ± 5	59 ± 2	72 ± 1	<LOQ (47)
K19.5	67 ± 3	±	<LOQ (25)	263 ± 3	308 ± 11	57 ± 9	62 ± 3	83 ± 4	<LOQ (47)
K20.0	88 ±4	±	<LOQ (25)	313 ± 9	337 ± 11	74 ± 8	55 ± 2	89 ± 3	<LOQ (47)
K21.5	89 ± 2	±	<LOQ (25)	353 ± 4	469 ± 20	86 ± 2	50 ± 1	97 ± 4	<LOQ (47)
	Top			Top			Top		
C0	38 ± 2			116 ± 2			<LOQ (47)		
C15	26 ± 3			106 ± 2			<LOQ (47)		
C20	27 ± 1			115 ± 1			<LOQ (47)		
C40	34 ± 2			138 ± 2			<LOQ (47)		
C50	39 ± 2			150 ± 3			<LOQ (47)		
Malt	65 ± 3			209 ± 3			<LOQ (47)		

SUPPLEMENTARY INFORMATION 3

Statistical evolution of free and cysteinylated Strecker aldehydes as a function of kilning time in samples collected from the bottom, middle and top layer of the kiln - malting batch A, malting batch B.

Compounds: 2MP = 2-methylpropanal, 2MB = 2-methylbutanal, 3MB = 3-methylbutanal, and PHE = phenylacetaldehyde. Methional is not presented as not most of values were <LOD. 2MP-CYS = cysteinylated 2-methylpropanal, 2MB-CYS= cysteinylated 2 methylbutanal, 3MB-CYS = cysteinylated 3-methylbutanal, and PHE-CYS = cysteinylated phenylacetaldehyde. Cysteinylated methional is not presented as not most of values were <LOD

Statistical comparisons between bottom, middle and top layer by post-hoc HSD Tukey's test to distinguish among significant different groups ($p \leq 0.05$) (a, b, c). x – statistical comparison not shown because quantification values are below LOD.

KILNING A

2MP

(h)	12	14	16	18	18.5	19	19.5	20	20.5	21	22
T	a	a	a	a	a	a	a	a	a	a	a
M	b	b	b	b	b	b	b	b	b	b	b
B	c	b	c	b	b	c	b	c	b	c	b

2MB

(h)	12	14	16	18	18.5	19	19.5	20	20.5	21	22
T	x	x	a	a	a	a	a	a	a	a	a
M	x	x	b	b	b	a	b	b	b	b	b
B	x	x	b	b	b	b	b	b	b	c	c

3MB

(h)	12	14	16	18	18.5	19	19.5	20	20.5	21	22
T	x	x	x	x	a	a	a	a	a	a	a
M	x	a	a	a	b	b	b	b	b	b	b
B	a	a	b	b	b	c	b	b	b	c	b

PHE

(h)	12	14	16	18	18.5	19	19.5	20	20.5	21	22
T	x	x	x	x	a	a	a	a	a	a	a
M	x	x	a	a	ab	a	b	b	b	b	b
B	x	x	a	a	b	b	b	b	b	b	b

KILNING B

2MP

(h)	12.5	13	13.5	14	14.5	15	15.5	16	16.5	17	17.5	18	18.5	19	19.5	20
T	a	a	a	a	a	a	a	a	a	a	a	a	a	a	a	a
M	ab	a	a	a	a	b	b	b	b	b	b	b	b	b	b	b
B	b	b	b	b	b	c	c	c	c	c	c	c	c	c	c	b

2MB

(h)	12.5	13	13.5	14	14.5	15	15.5	16	16.5	17	17.5	18	18.5	19	19.5	20
T	a	a	a	a	a	a	a	a	a	a	a	a	a	a	x	a
M	b	b	b	b	b	b	b	b	b	b	b	b	b	b	a	**b**
B	c	c	c	c	c	c	c	c	c	c	c	c	b	c	b	c

3MB

(h)	12.5	13	13.5	14	14.5	15	15.5	16	16.5	17	17.5	18	18.5	19	19.5	20
T	a	a	a	a	a	a	a	a	a	a	a	a	a	a	x	a
M	b	a	a	b	b	b	b	b	b	b	b	b	b	b	a	**b**
B	c	b	b	c	c	c	c	c	b	c	c	c	c	c	b	c

PHE

(h)	12.5	13	13.5	14	14.5	15	15.5	16	16.5	17	17.5	18	18.5	19	19.5	20
T	a	a	a	a	a	a	a	a	a	a	a	a	a	a	x	a
M	b	b	b	b	b	b	b	b	b	b	b	b	b	b	a	b
B	c	b	b	b	c	b	b	b	b	b	b	c	b	c	b	c

Figure S3.1. Statistical evolution of free Strecker aldehydes as a function of kilning time in samples collected from the bottom (B), middle (M) and top (T) layer of the kiln - malting batch A (left side), malting batch B (right side).

KILNING A

2MP-CYS

(h)	12	14	16	18	18.5	19	19.5	20	20.5	21	22
T	x	x	x	x	x	x	x	x	x	a	a
M	x	a	a	a	a	a	a	a	a	b	b
B	a	b	b	b	b	b	b	b	b	c	b

2MB-CYS

(h)	12	14	16	18	18.5	19	19.5	20	20.5	21	22
T	x	x	x	x	x	x	x	x	x	a	a
M	x	x	x	x	a	a	a	a	a	b	b
B	x	x	x	a	a	a	a	b	a	c	b

3MB-CYS

(h)	12	14	16	18	18.5	19	19.5	20	20.5	21	22
T	x	x	x	x	x	x	x	a	a	a	a
M	x	x	x	a	a	a	a	b	b	b	b
B	a	a	a	b	b	b	b	c	b	c	c

PHE-CYS

(h)	12	14	16	18	18.5	19	19.5	20	20.5	21	22
T	x	x	x	x	x	x	x	a	a	a	a
M	x	x	x	a	a	a	a	b	b	b	b
B	x	x	x	b	b	a	a	b	b	b	b

KILNING B

2MP-CYS

(h)	12.5	13	13.5	14	14.5	15	15.5	16	16.5	17	17.5	18	18.5	19	19.5
T	x	x	x	a	a	a	a	a	a	a	a	a	a	a	a
M	x	x	x	b	b	b	b	b	b	b	b	b	b	b	b
B	x	x	x	c	c	c	c	c	c	c	c	b	c	c	b

2MB-CYS

(h)	12.5	13	13.5	14	14.5	15	15.5	16	16.5	17	17.5	18	18.5	19	19.5
T	x	x	a	a	a	a	a	a	a	a	a	a	a	a	a
M	x	x	a	a	a	a	a	a	a	a	a	b	b	b	b
B	x	x	b	b	b	b	b	b	b	b	b	c	c	c	c

3MB-CYS

(h)	12.5	13	13.5	14	14.5	15	15.5	16	16.5	17	17.5	18	18.5	19	19.5
T	a	a	a	a	a	a	a	a	a	a	a	a	a	a	a
M	a	a	b	b	b	b	b	b	b	b	b	b	b	b	b
B	b	b	c	c	c	c	c	c	c	c	c	b	c	c	b

PHE-CYS

(h)	12.5	13	13.5	14	14.5	15	15.5	16	16.5	17	17.5	18	18.5	19	19.5
T	a	a	a	a	a	a	a	a	a	a	a	a	a	a	a
M	a	b	b	b	b	b	b	b	b	b	b	b	b	b	b
B	b	c	b	c	b	c	c	c	c	c	c	c	b	c	c

Figure S3.2. Statistical evolution of cysteinylated Strecker aldehydes as a function of kilning time in samples collected from the bottom (B), middle (M) and top (T) layer of the kiln - malting batch A (left side), malting batch B (right side).

SUPPLEMENTARY INFORMATION 4

Evolution of free and cysteinylated Strecker aldehydes in relation the grain drying process and applied heat load during kilning. Samples collected from bottom, middle and top grain bed layer of batch A and batch B.

Compounds: 2MP = 2-methylpropanal, 2MB = 2-methylbutanal, 3MB = 3-methylbutanal, MET = methional, PHE = phenylacetaldehyde, 2MP-CYS = cysteinylated 2-methylpropanal, 2MB-CYS= cysteinylated 2-methylbutanal, 3MB-CYS = cysteinylated 3-methylbutanal, MET-CYS = cysteinylated methional and PHE-CYS = cysteinylated phenylacetaldehyde.

Results are expressed as mean values (n=3 for aldehydes, n=2 for moisture content and TBI), error bars = standard deviation. Statistical comparisons between bottom, middle and top layer by post-hoc HSD Tukey's test to distinguish among significant different groups ($p \leq 0.05$) (a, b, c). x – statistical comparison not shown because quantification values are below LOD.

BOTTOM LAYER

FREE ALDEHYDES

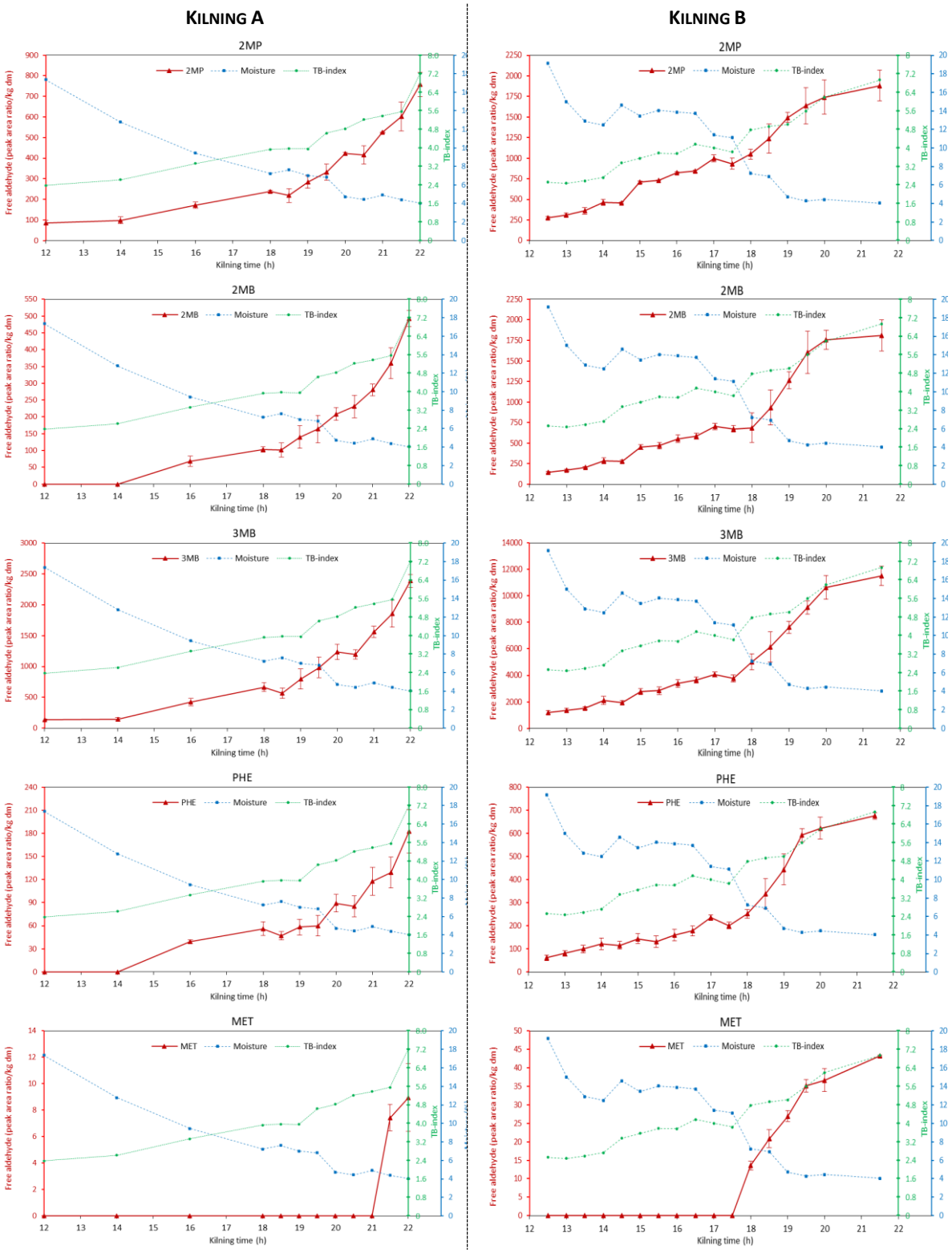

Figure S4.1. Evolution of free Strecker aldehydes in relation to the grain drying process and applied heat load during kilning. Samples collected from the bottom layer.

BOTTOM LAYER

CYSTEINYLATED ALDEHYDES

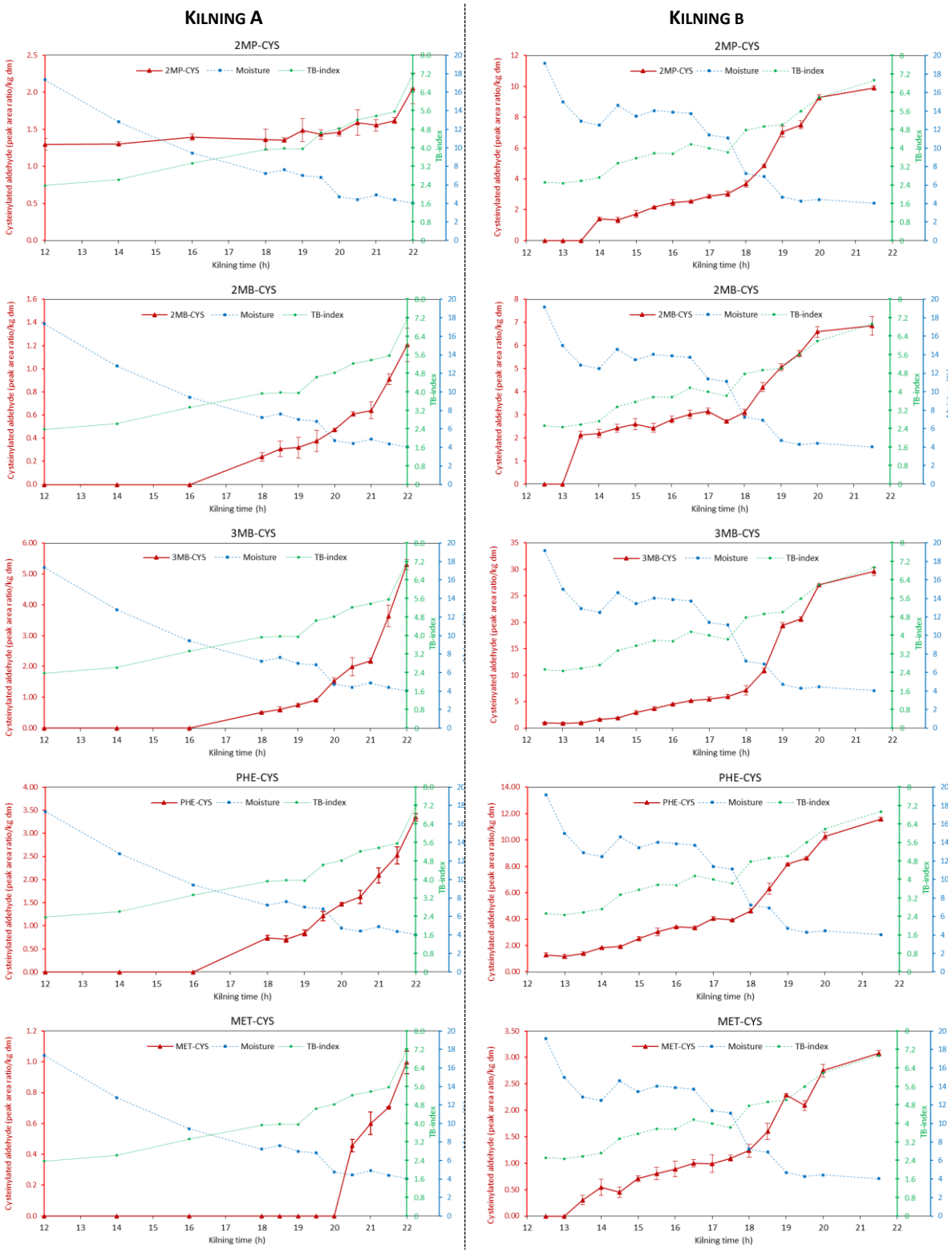

Figure S4.2. Evolution of cysteinylated Strecker aldehydes in relation to the grain drying process and applied heat load during kilning. Samples collected from the bottom layer.

MIDDLE LAYER

FREE ALDEHYDES

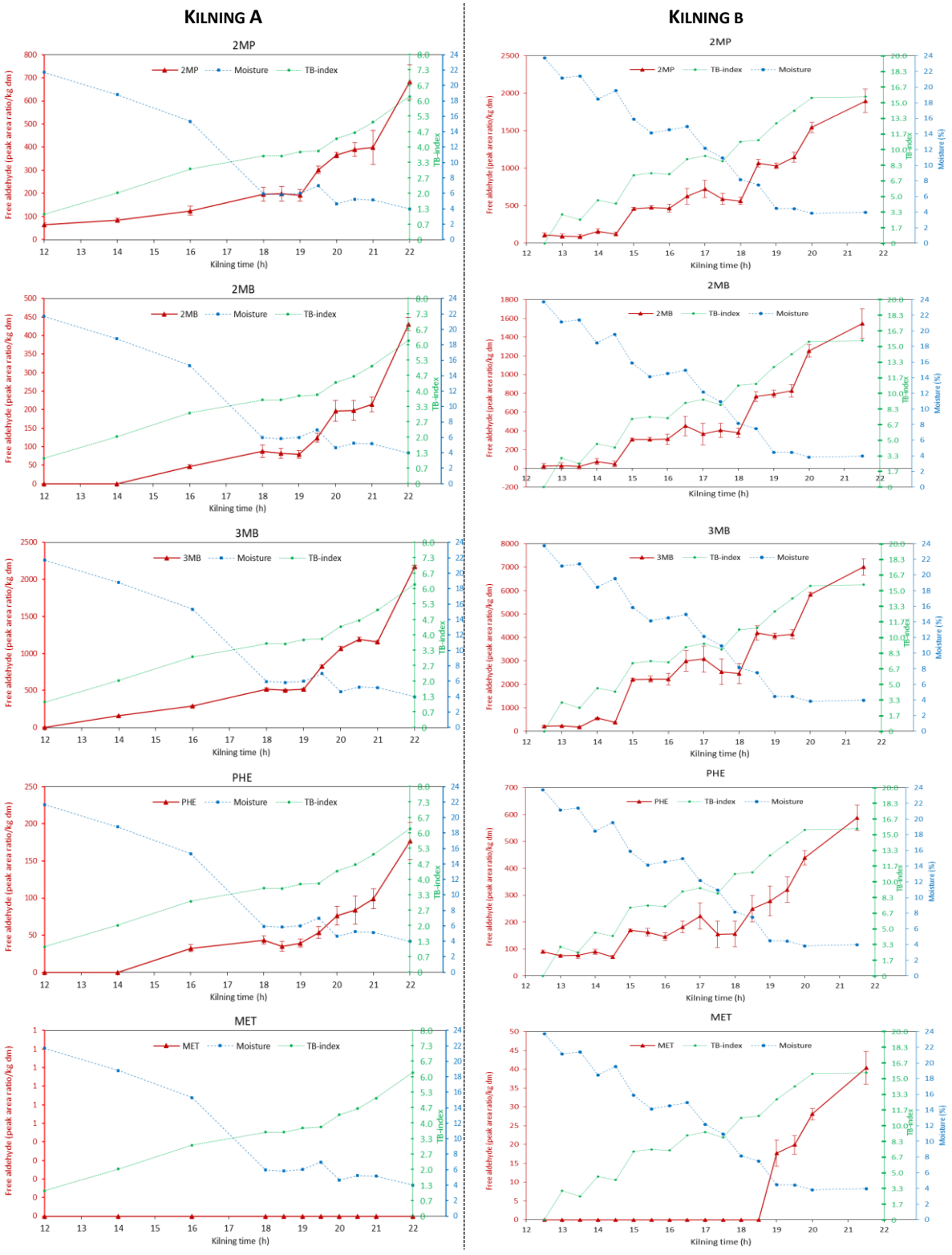

Figure S4.3 Evolution of free Strecker aldehydes in relation to the grain drying process and applied heat load during kilning. Samples collected from the middle layer.

MIDDLE LAYER

CYSTEINYLATED ALDEHYDES

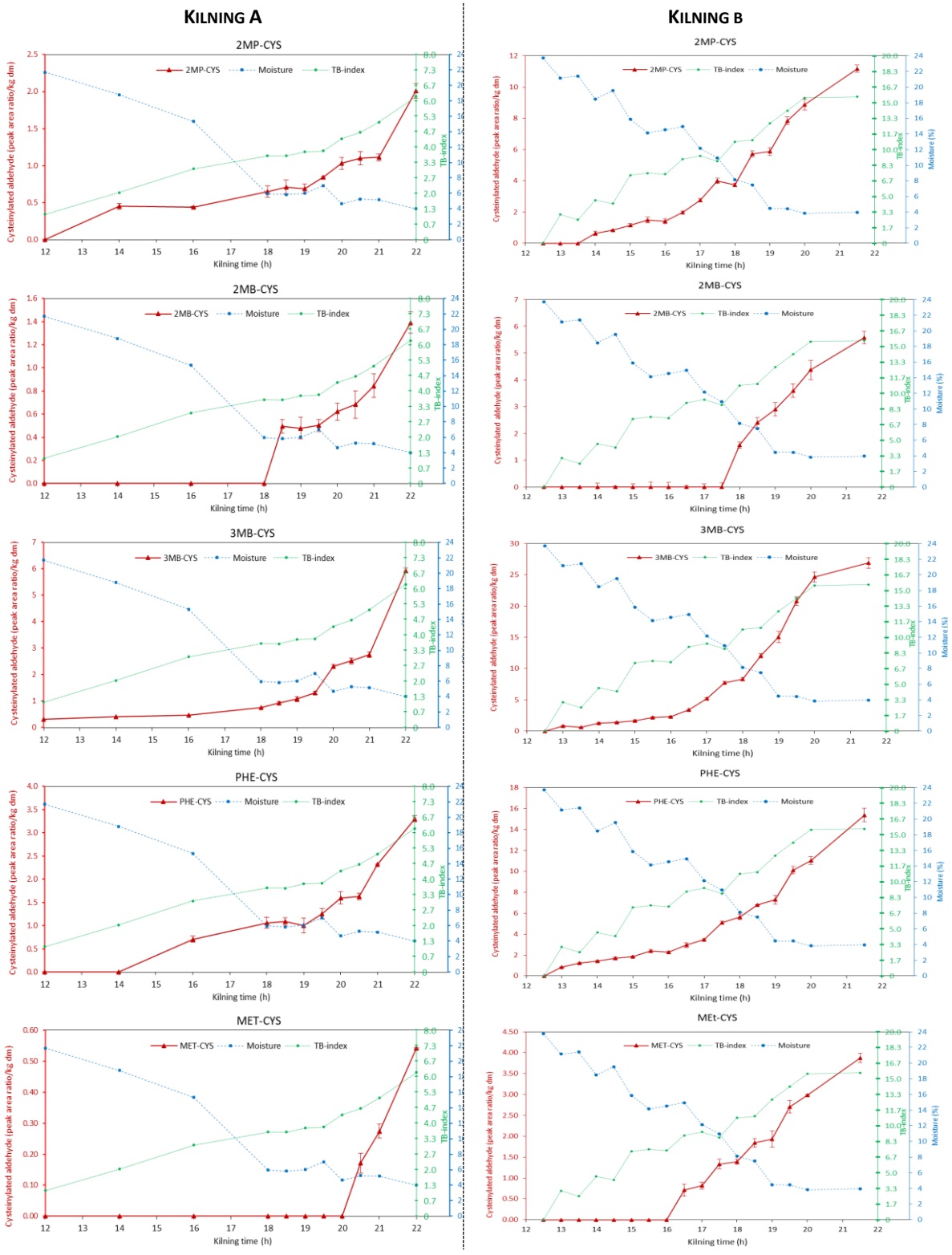

Figure S4.4 Evolution of cysteinylated Strecker aldehydes in relation to the grain drying process and applied heat load during kilning. Samples collected from the middle layer.

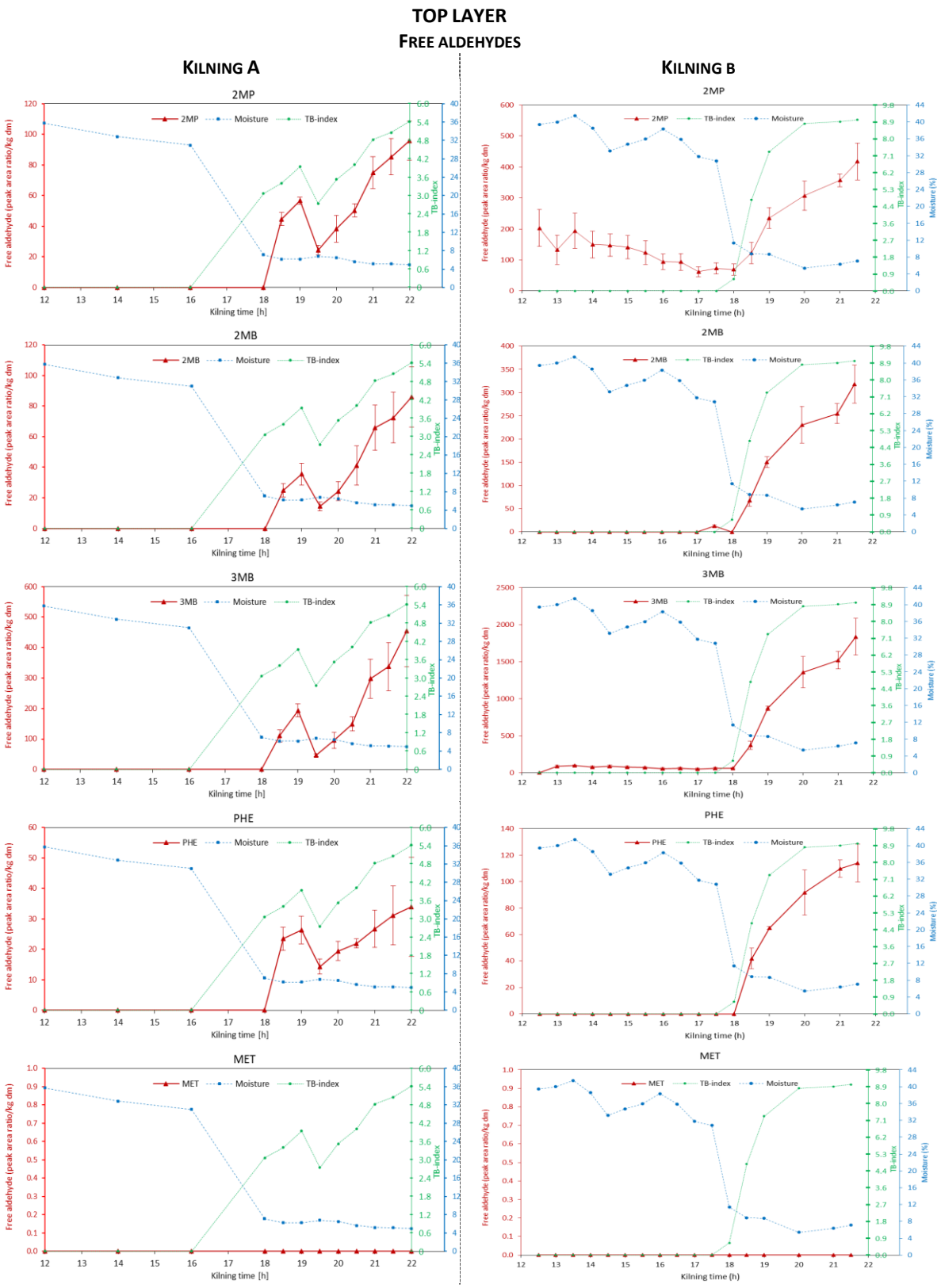

Figure S4.5 Evolution of free Strecker aldehydes in relation to the grain drying process and applied heat load during kilning. Samples collected from the top layer.

TOP LAYER

CYSTEINYLATED ALDEHYDES

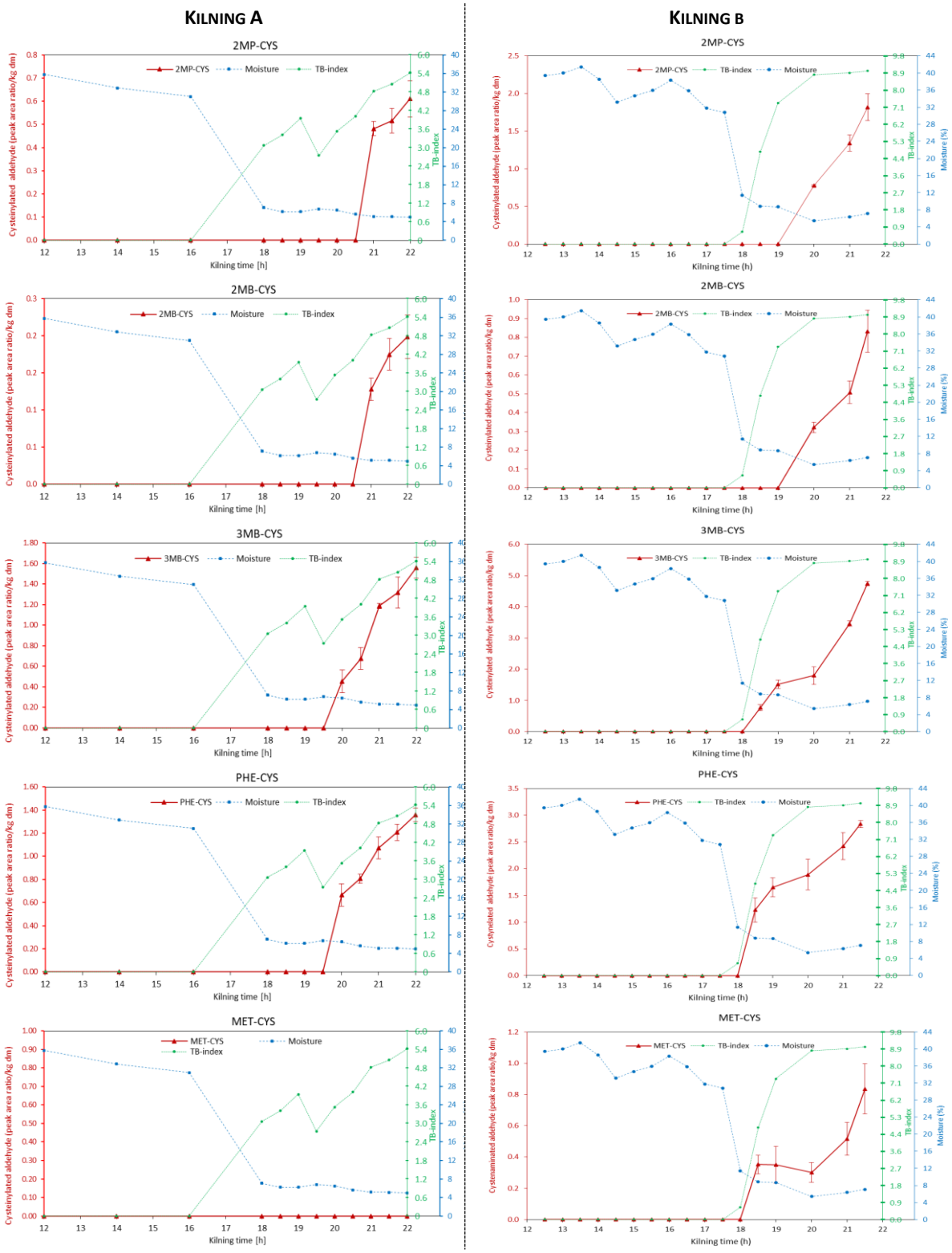

Figure S4.6 Evolution of cysteinylated Strecker aldehydes in relation to the grain drying process and applied heat load during kilning. Samples collected from the top layer.