Supporting Information S2: Tables and Figures

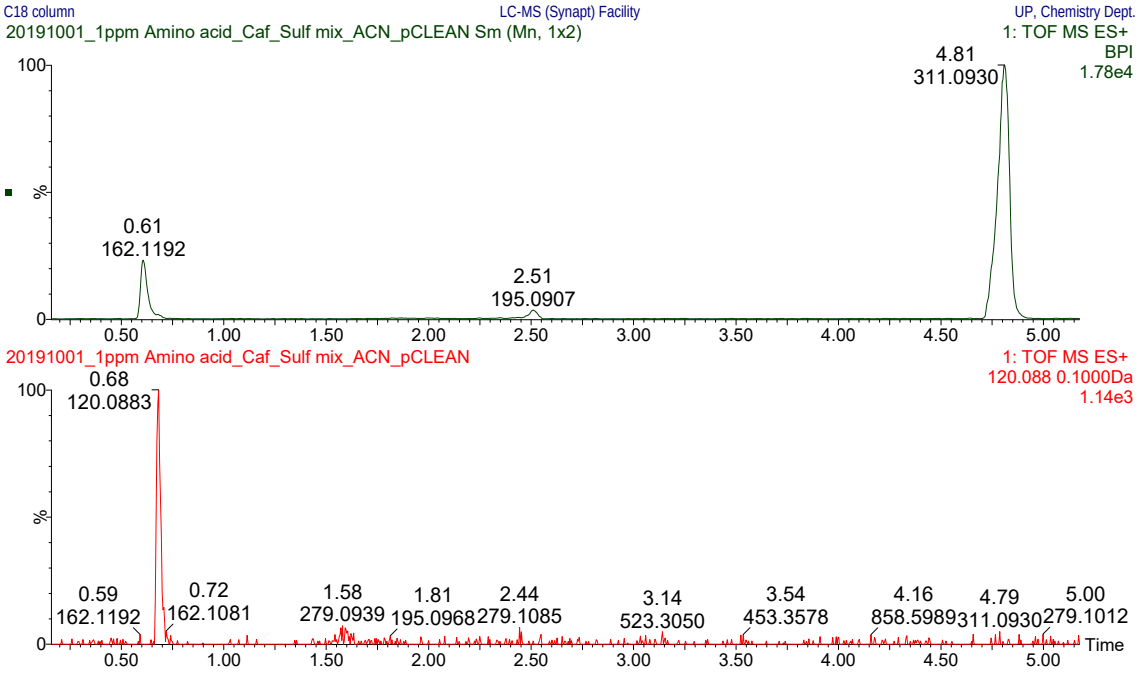

Figure S-1. Base peak ion (BPI) chromatogram of the selected analytes, L-carnitine (162.1192 *m/z* $[M+H]^+$), caffeine (195.0907 *m/z* $[M+H]^+$) and sulfadimethoxine (311.0930 *m/z* $[M+H]^+$) using the BEH C_{18} column (top). Extracted ion chromatogram (EIC) for L-phenylalanine at 120.0883 *m/z* ($[M\text{-}COOH]^+$) indicating the presence of the analyte when using the BEH C_{18} column (bottom). Compounds from a 1 ng/µl (5 µl injection) mixture were analysed using ESI+ mode with UPLC-TOFMS.

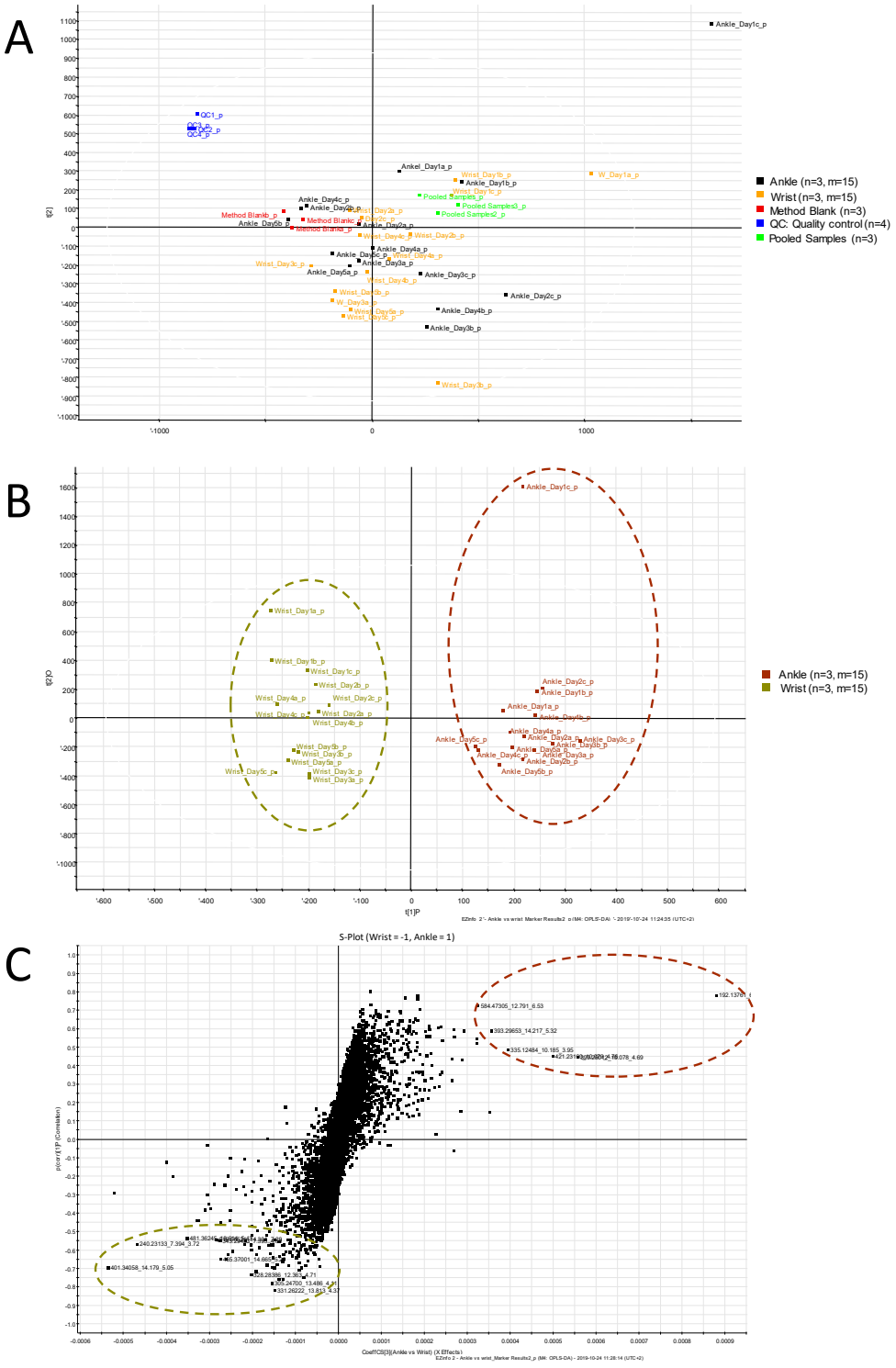

Figure S-2. (A) PCA score plot showing no distinct clustering between the two skin regions sampled. (B) OPLS-DA score plot using ESI positive mode UPLC-IMS-HRMS data, over 16000 markers, revealing separation between the ankle (red) and wrist (green) skin surface chemical profiles. (C) S-plot showing *m/z*, retention time (min) and drift time (ms) pairs of compounds contributing the differences in the chemical profiles of the ankle (red) and wrist (green) skin surface area.

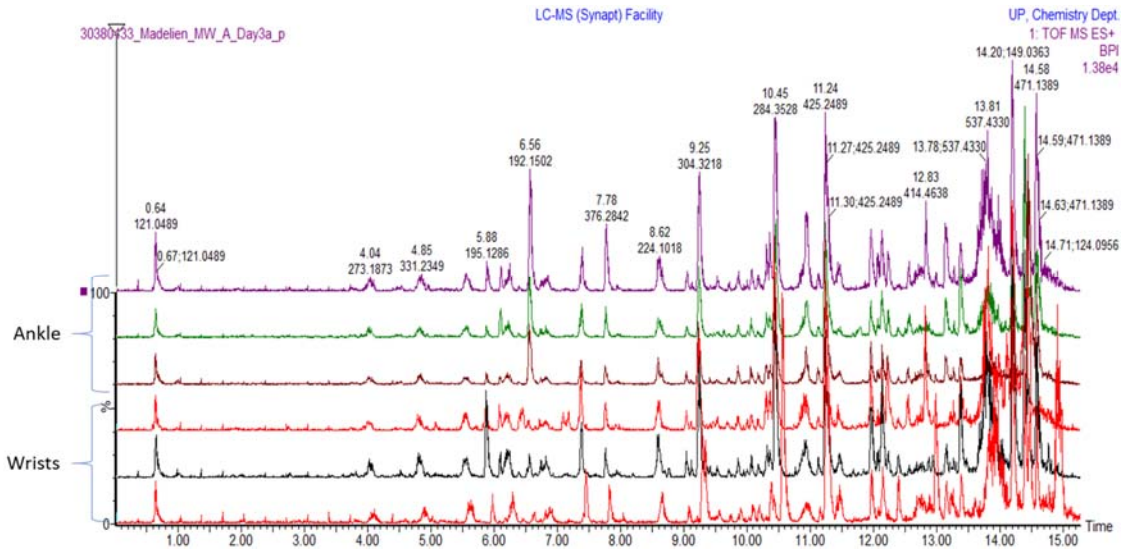

Figure S-3. Base peak ion (BPI) chromatograms showing two skin regions sampled on Day 3. Three repeats per surface skin area sampled are shown. The top three traces are from the ankle skin surface area sampled and the lower three traces is from the wrist skin surface area sampled.

Table S-1: Compounds, tentatively identified during an untargeted analysis of the human skin surface, detected on the ankle and wrist skin surface area using a passive sampling method and solvent desorption with UPLC-IMS-HRMS. The compounds listed were classified, using chemometric techniques, as contributing to the difference between the ankle and wrist skin surface chemical profile. Mean, median and range are given in terms of detector counts.

										Ankle (m=15)[5]					Wrist (m=15)[5]				
													Range					Range	
#	Compound	Compound class	*m/z*[1] (Da) (mass error (ppm))	Adducts	RT[2] (min)	CCS[3] (Å^2) (CCS % error)[4]	Fragments (*m/z*) (mass error (ppm))	Database	Marker	Count (n=5)[6]	Mean	Median	Min	Max	Count (n=5)[6]	Mean	Median	Min	Max
1	1-Phenyl-1,3-hexadecanedione	Alkyl-phenylketone	331.1431 (5.9)	$[M+H]^+$	13.82	192.9 (2.9)	-	HMDB	Wrist	5	39	25	22	66	5	57	67	20	83
2	1-(4-Anilinophenyl)-3-morpholin-4-ylthiourea	Nitrogen containing	327.1286 (0.4)	$[M-H]^-$	12.01	179.9 (-0.5)	-	ChemSpider	Wrist	5	179	183	84	251	5	281	261	231	386
3	2-Benzylamino-3-[(E)-benzylimino-methyl]-7-methyl-pyrido[1,2-a]pyrimidin-4-one	Nitrogen containing ketone	381.1741 (5.4)	$[M-H]^-$	13.39	192.8 (1.5)	183.0136 (-96.2)	ChemSpider	Wrist	5	997	1050	613	1297	5	1333	1199	1047	2005
4	3-[(5-Isobutyl-1,2,3,4-tetrahydropyrimido[4',5':4,5] thieno[2,3-c]isoquinolin-8-yl)amino]-1-propanol	Nitrogen containing alcohol	369.1751 (-0.8)	$[M-H]^-$	13.56	190.6 (2.6)	311.1677 (28.9) 326.1890 (59.3) 355.1603 (1.4)	ChemSpider	Wrist	5	272	311	169	328	5	485	472	353	730
5	4-(1H-Indol-3-yl)-1-(4-isobutyryl-1-piperazinyl)-1-butanone	Nitrogen containing ketone	340.2044 (3.9)	$[M-H]^-$	11.85	189.8 (-1.4)	311.1683 (14.2) 326.1844 (-9.2)	ChemSpider	Ankle	2	91	91	40	142	n.d.[6]	-	-	-	-
6	4-[4-(4-Methoxyphenyl)-1-piperazinyl]-5,6-dimethylthieno[2,3-d]pyrimidine	Nitrogen containing	353.1440 (-0.4)	$[M-H]^-$	12.38	184.35 (3.8)	-	ChemSpider	Wrist	5	326	346	202	401	5	559	496	467	842
7	5,6-trans-25-Hydroxyvitamin D3	Vitamin D3 derivative	401.3406 (-2.0)	$[M+H]^+$	14.18	210.6 (0.2)	81.0705 (7.3) 95.0848 (-7.3) 133.1028 (12.5) 145.1007 (-3.4) 157.1021 (6.1) 159.1145 (-14.6) 175.1089 (-16.4) 253.1947 (-1.5) 365.3192 (-1.1) 383.3275 (-8.8)	HMDB	Wrist	5	291	312	73	463	5	1013	1002	739	1297

8	11-(2-Sulfophenyl)undecanoic acid	Carboxylic acid (sulphur containing)	341.1431 (0.8)	$[M-H]^-$	12.65	183.9 (-1.3)	184.0194 (-3.2) 297.1521 (-3.0)	ChemSpider	Wrist	5	195	176	101	296	5	341	325	253	514
9	Allochenodeoxycholic acid	Bile acid	393.2980 (-5.0)	$[M+H]^+$	14.22	218.9 (-6.1)	283.2622 (-3.3) 301.2457 (-22.9) 297.2149 (-21.5)	HMDB	Ankle	5	648	463	82	1610	5	61	52	9	117
10	Brassinolide	Brassinolides and derivatives	481.3543 (4.0)	$[M+H]^+$	13.46	217.9 (1.2)	428.3294 (2.2) 441.3209 (-0.3) 445.3280 (-7.3)	HMDB	Wrist	5	138	144	92	170	5	231	202	116	385
11	Capparilloside A	Phenol glycoside	335.1243 (1.5)	$[M+H]^+$	10.18	178.22 (-0.8)	-	HMDB	Ankle	3	619	256	157	1445	n.d.	-	-	-	-
12	Ceramide (d18:1/20:0)	Long chain ceramide	616.5653 (2.2)	$[M+Na]^+$	14.15	276.2 (-3.1)	255.2327 (3.4) 283.2623 (-2.9)	HMDB	Wrist	5	29	26	1	53	4	336	287	52	719
13	Ethyl 1-[(3-ethoxy-3-oxopropyl)carbamoyl]-4-(tetrahydro-2H-pyran-2-ylmethyl)-4-piperidinecarboxylate	Nitrogen containing ester	399.2501 (2.9) 421.2318 (0.71)	$[M+H]^+$ $[M+Na]^+$	10.08	199.5 (-3.33) 201.4 (-1.9)	55.0547 (8.9) 57.0700 (1.3) 101.0941 (-19.8) 225.0863 (-3.3) 241.1733 (25.1) 243.0949 (-10.8) 299.1604 (0.8) 321.1419 (-8.2)	ChemSpider	Ankle	4	1973	796	78	6224	1	289	289	289	289
14	Margaroylglycine	n-Acyl-alpha amino acids	328.2847 (0.3) 326.2716 (4.7)	$[M+H]^+$ $[M-H]^-$	12.38	201.7 (-4.6) 186.4 (0.0)	282.2806 (1.2)	HMDB	Wrist	5	26	30	5	39	5	166	158	130	209
15	N-(3-Aminopropyl)-N-isopropylmethanesulfonamide	Nitrogen and sulphur containing	193.1014 (-1.0)	$[M-H]^-$	5.81	148.8 (-5.3)	-	ChemSpider	Ankle	5	767	642	179	1772	4	598	419	315	1239
16	N-(3-Butoxypropyl)-N'-(2-ethylhexyl)succinamide	Nitrogen containing	343.2949 (-1.9) 365.2765 (-4.1)	$[M+H]^+$ $[M+Na]^+$	7.38	200.69 (-3.0) 202.24 (-2.3)	126.0537 (-9.7)	ChemSpider	Wrist	5	194	221	29	326	5	585	494	161	1079
17	N,N-Diethylbenzeneacetamide	Nitrogen containing	192.1382 (-0.5)	$[M+H]^+$	6.56	144.1 (0.3)	72.0445 (2.1) 91.0540 (-2.6) 100.0754 (-2.6) 119.0486 (-4.8)	HMDB	Ankle	5	2856	2396	1418	5000	5	331	267	237	450
18	N-Cyclooctylheptanamide	Nitrogen containing	240.2316 (-2.4)	$[M+H]^+$	7.37	173.7 (-4.4)	57.0712 (22.6) 81.0701 (2.7)	ChemSpider	Wrist	5	558	551	75	943	5	1487	1413	660	2373
19	Obtusifoliol	Terpene	465.3700 (-0.7)	$[M+Na]^+$	14.57	215.9 (-5.1)	425.3752 (-6.1)	HMDB	Wrist	5	156	144	122	211	5	386	418	249	456
20	Oleyl acetate	Fatty alcohol esters	311.2954 (3.0)	$[M+H]^+$	14.30	198.5 (-3.1)	-	HMDB	Ankle	5	58	62	14	104	5	47	44	13	106
21	Pentadecanoylglycine	n-Acyl-alpha amino acids	298.2408 (6.8)	$[M-H]^-$	11.01	178.1 (0.9)	254.2497 (2.9)	HMDB	Wrist	4	49	45	25	79	5	152	143	65	244
22	Sideridiol	Terpene	305.2476 (0.2)	$[M+H]^+$	13.48	182.7 (-4.3)	93.0700 (1.6)	HMDB	Wrist	5	48	35	20	82	5	51	55	21	95
23	Tridecanoylglycine	n-Acyl-alpha amino acids	270.2088 (5.0)	$[M-H]^-$	9.54	170.9 (1.7)	226.2199 (9.8)	HMDB	Wrist	5	37	42	8	62	5	134	119	66	259

[1]*m/z*: mass-to-charge ratio
[2]RT: retention time
[3]CCS: collision cross section
[4]CCS error between experimental and modelled value
[5]Number of measurements taken

[6]Number of days (n=5) compound was detected
[7]n/a: not available
[8]Not detected