Supplementary Materials

for the manuscript by Schuhmann et al “Shotgun Lipidomics on a LTQ Orbitrap Mass Spectrometer by Successive Switching between Acquisition Polarity Modes”

Content:

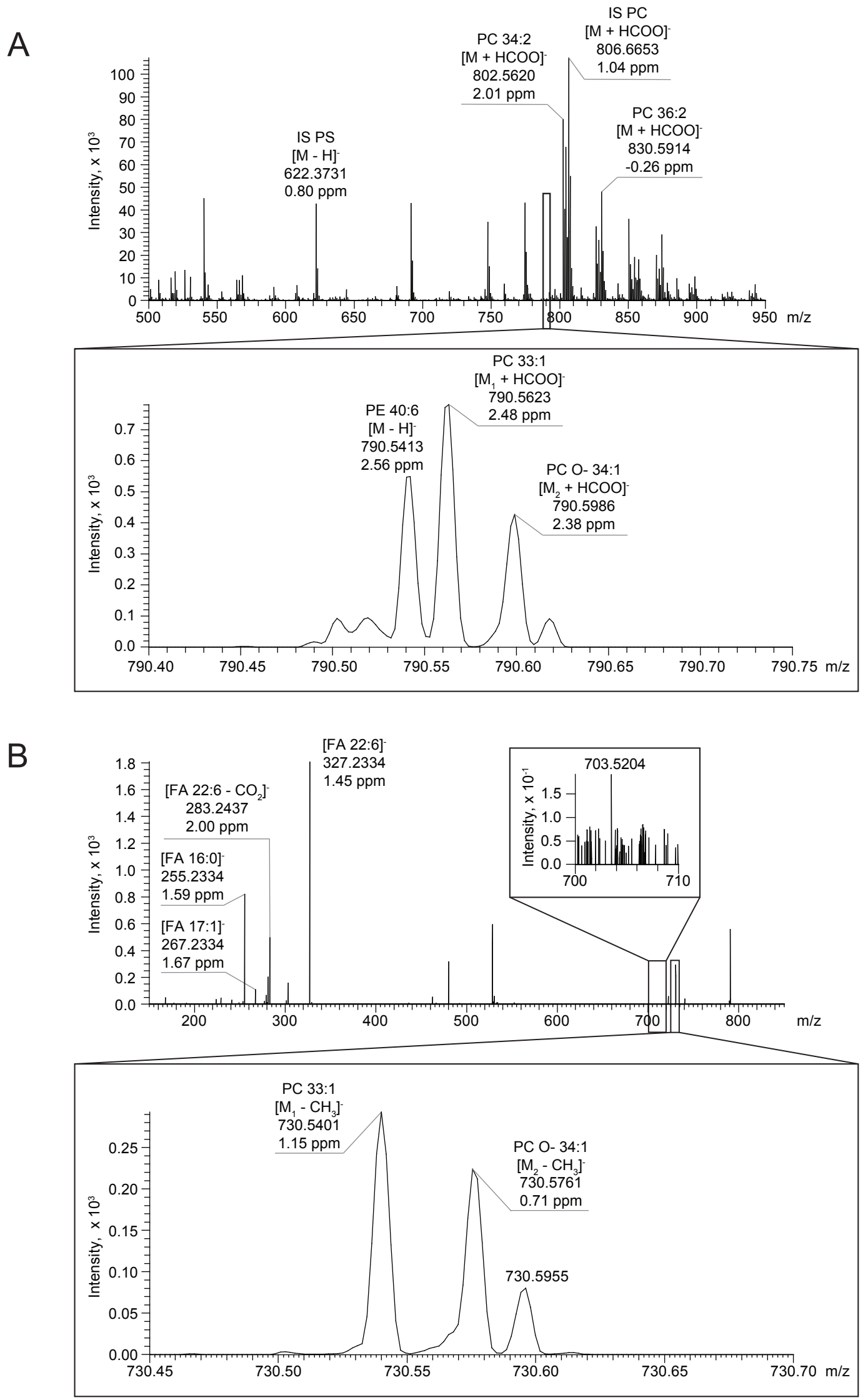
A
IS PC
[M + HCOO]-
806.6653
1.04 ppm
PC 34:2
[M + HCOO]-
802.5620
2.01 ppm
PC 36:2
[M + HCOO]-
830.5914
-0.26 ppm
IS PS
[M - H]-
622.3731
0.80 ppm
Intensity, x 10^3
m/z
PC 33:1
[M1 + HCOO]-
790.5623
2.48 ppm
PE 40:6
[M - H]-
790.5413
2.56 ppm
PC O- 34:1
[M2 + HCOO]-
790.5986
2.38 ppm
B
[FA 22:6]-
327.2334
1.45 ppm
[FA 22:6 - CO2]-
283.2437
2.00 ppm
[FA 16:0]-
255.2334
1.59 ppm
[FA 17:1]-
267.2334
1.67 ppm
703.5204
Intensity, x 10^-1
PC 33:1
[M1 - CH3]-
730.5401
1.15 ppm
PC O- 34:1
[M2 - CH3]-
730.5761
0.71 ppm
730.5955

Figure S1. HCD FT MS/MS confirms the presence of PC species with odd numbered fatty acids in human blood plasma. (A) FT-MS of a blood plasma total lipid extract; zoomed region shows precursors of PE 40:6, PC O- 34:1 and PC 33:1 that has the same *m/z* as or PS 36:0. (B) HCD FT-MS/MS of m/z 790.5623 precursor; products of demethylation (neutral loss of $C_2 H_4 O_2$ (Δ*m/z* 60.0211) is specific to species with the choline head group) of PC 33:1 and PC O- 34:1 precursors are boxed and corresponding zoomed region is shown in the inset below.

Considering the detected fragments of acyl anion and losses of fatty acid ketens, possible PC species are:

PC 15:0 / 18:1 ($[M_1 – CH_3 – FA\ 18:1]^-$ at *m/z* 466.2943 (0.79 ppm); $[FA\ 18:1]^-$ at *m/z* 281.2491 (1.69 ppm); $[FA\ 15:0]^-$ at *m/z* 241.2176 (1.23 ppm));

PC 16:0 / 17:1 ($[M_1 – CH_3 – FA\ 16:0]^-$ at *m/z* 492.3100 (0.91 ppm); $[FA\ 17:1]^-$ at *m/z* 267.2334 (1.67 ppm); $[FA\ 16:0]^-$ at *m/z* 255.2334 (1.59 ppm)).

PC O- 34:1 ($[M_2 – CH_3 – FA\ 18:1]^-$ at *m/z* 466.3307 (0.93 ppm); $[FA\ 18:1]^-$ at *m/z* 281.2491 (1.69 ppm)).

At the same time, fragments specific for PS 36:0 – the expected neutral loss of $C_3 H_5 O_2 N$ (Δ *m/z* 87.032; zoomed at the inset) and $[M_1 – C_3 H_5 O_2 N – FA\ 18:0]$ – were undetectable with a mass tolerance less than 10 ppm. We therefore concluded that PS 36:0 was not present in these plasma samples.

MS and MS/MS spectra were acquired in the profile mode under operator control on LTQ Orbitrap Velos instrument as described in (Schuhmann et al. (2011) Anal Chem 83, 5480-5487.). However, FT MS and HCD FT MS/MS spectra were both acquired at the target mass resolution of $R_{m/z\ 400}$ = 100,000. Maximum injection time for HCD FT-MS/MS was set to 8 s.

Table S1. Lipid species identified in a polar bovine heart extract.

.

Lipid class	Lipid species	*m/z* * positive mode	*m/z* * negative mode	Mass accuracy, ppm positive mode	Mass accuracy, ppm negative mode
		$[M + NH_4]^+$			
Cholesteryl ester	CholE 18:1	668.6339		-0.16	
	CholE 18:2	666.6183		-0.02	
		$[M + NH_4]^+$	$[M + HCOO]^-$		
Triacylglycerol	TAG 36:0	656.5823		-0.15	
	TAG 38:0	684.6137		0.12	
	TAG 40:0	712.6451		0.17	
	TAG 40:1	710.6294		0.18	
	TAG 42:0	740.6764		0.23	
	TAG 42:1	738.6608		0.28	
	TAG 42:2	736.6450		0.11	
	TAG 43:0	754.6920		0.09	
	TAG 43:1	752.6762		-0.05	
	TAG 44:0	768.7075		-0.02	
	TAG 44:1	766.6920		0.12	
	TAG 44:2	764.6764		0.14	
	TAG 45:0	782.7233		0.14	
	TAG 45:1	780.7076		0.09	
	TAG 46:0	796.7389		0.00	
	TAG 46:1	794.7233		0.12	
	TAG 46:2	792.7077		0.19	
	TAG 46:3	790.6922		0.35	
	TAG 47:0	810.7547		0.21	
	TAG 47:1	808.7391		0.31	
	TAG 47:2	806.7235		0.32	
	TAG 48:0	824.7699	851.7339	-0.28	-0.81
	TAG 48:1	822.7544	849.7181	-0.12	-0.94
	TAG 48:2	820.7391	847.7018	0.29	-1.70
	TAG 48:3	818.7236		0.47	
	TAG 49:0	838.7859	865.7494	0.13	-0.92
	TAG 49:1	836.7704	863.7336	0.23	-1.09
	TAG 49:2	834.7549	861.7174	0.42	-1.78
	TAG 49:3	832.7393		0.46	
	TAG 50:0	852.8011	879.7651	-0.49	-0.84
	TAG 50:1	850.7855	877.7494	-0.34	-0.92
	TAG 50:2	848.7702	875.7337	0.00	-0.94
	TAG 50:3	846.7545	873.7174	-0.08	-1.67
	TAG 50:4	844.7394		0.60	
	TAG 51:0	866.8169	893.7808	-0.20	-0.76
	TAG 51:1	864.8014	891.7654	-0.07	-0.55
	TAG 51:2	862.7860	889.7496	0.18	-0.64
	TAG 51:3	860.7705	887.7334	0.43	-1.27
	TAG 51:4	858.7541		-0.51	

Lipid class	Lipid species	*m/z* *		Mass accuracy, ppm	
		positive mode	negative mode	positive mode	negative mode
Triacylglycerol	TAG 52:1	878.8147	905.7797	-2.79	-2.03
	TAG 52:2	876.8007	903.7645	-0.89	-1.54
	TAG 52:3	874.7856	901.7491	-0.20	-1.22
	TAG 52:4	872.7705	899.7338	0.38	-0.87
	TAG 52:5	870.7546		0.08	
	TAG 53:0	894.8474	921.8116	-1.14	-1.32
	TAG 53:1	892.8321	919.7962	-0.76	-0.97
	TAG 53:2	890.8165	917.7805	-0.67	-1.06
	TAG 53:3	888.8011	915.7650	-0.39	-0.88
	TAG 53:4	886.7850		-0.95	
	TAG 54:1	906.8472	933.8111	-1.31	-1.86
	TAG 54:2	904.8316	931.7954	-1.26	-1.88
	TAG 54:3	902.8165	929.7801	-0.67	-1.54
	TAG 54:4	900.8012	927.7647	-0.27	-1.23
	TAG 54:5	898.7855	925.7495	-0.35	-0.75
	TAG 54:6	896.7694		-0.88	
	TAG 55:1	920.8635	947.8275	-0.65	-1.01
	TAG 55:2	918.8479	945.8117	-0.57	-1.19
	TAG 55:3	916.8323	943.7960	-0.54	-1.21
	TAG 55:4	914.8162		-1.04	
	TAG 55:5	912.8036		2.34	
	TAG 56:1	934.8794		-0.38	
	TAG 56:2	932.8637	959.8276	-0.35	-0.86
	TAG 56:3	930.8481	957.8117	-0.33	-1.12
	TAG 56:4	928.8324	955.7962	-0.37	-0.99
	TAG 56:5	926.8167	953.7806	-0.40	-0.90
	TAG 56:6	924.8010	951.7649	-0.50	-0.98
	TAG 57:1	948.8950		-0.37	
	TAG 57:2	946.8797		0.00	
	TAG 57:3	944.8638		-0.24	
	TAG 57:5	940.8326		-0.21	
	TAG 58:1	962.9107		-0.34	
	TAG 58:2	960.8954		0.06	
	TAG 58:3	958.8798		0.06	
	TAG 58:4	956.8638		-0.32	
	TAG 58:5	954.8484	981.8122	-0.06	-0.57
	TAG 58:6	952.8328	979.7964	0.03	-0.81
	TAG 60:2	988.9269		0.24	
	TAG 60:3	986.9103		-0.74	

Lipid class	Lipid species	*m/z* *		Mass accuracy, ppm	
		positive mode	negative mode	positive mode	negative mode
		$[M + NH_4]^+$	$[M + HCOO]^-$		
Diacylglycerol	DAG 28:0		557.4425		0.44
	DAG 30:0		585.4738		0.36
	DAG 30:1	556.4934	583.4582	-0.25	0.39
	DAG 31:0		599.4893		0.08
	DAG 31:1		597.4738		0.29
	DAG 32:0		613.5050		0.18
	DAG 32:1		611.4894		0.24
	DAG 32:2	582.5090	609.4737	-0.41	0.16
	DAG 33:0		627.5206		0.04
	DAG 33:1		625.5050		0.25
	DAG 33:2		623.4894		0.26
	DAG 34:1	612.5557	639.5206	-0.75	0.09
	DAG 34:2	610.5405	637.5051	-0.08	0.35
	DAG 34:3		635.4895		0.42
	DAG 35:0		655.5516		-0.32
	DAG 35:1		653.5362		0.05
	DAG 35:2		651.5206		0.10
	DAG 36:1	640.5874	667.5516	-0.09	-0.27
	DAG 36:2	638.5717	665.5361	-0.13	-0.05
	DAG 36:3		663.5206		0.14
	DAG 36:4		661.5051		0.35
	DAG 37:1		681.5676		0.19
	DAG 37:2		679.5517		-0.20
	DAG 38:1		695.5831		-0.02
	DAG 38:2		693.5676		0.12
	DAG 38:3		691.5519		0.06
	DAG 38:4		689.5363		0.14
		$[M + NH_4]^+$	$[M + HCOO]^-$		
Monoacylglycerol	MAG 18:1		401.2910		0.22
	MAG 20:4		423.2754		0.48
	MAG 22:5		449.2911		0.51
		$[M + H]^+$	$[M + HCOO]^-$		
Ceramide	Cer 34:1:1		582.5105		0.32
	Cer 36:1:1		610.5418		0.33
	Cer 36:2:1		608.5261		0.19
	Cer 40:1:1		666.6042		-0.04
	Cer 41:1:1		680.6198		-0.04
	Cer 41:2:1		678.6042		-0.02
	Cer 42:1:1		694.6356		0.12
	Cer 42:2:1		692.6199		0.12

Lipid class	Lipid species	*m/z* * positive mode	*m/z* * negative mode	Mass accuracy, ppm positive mode	Mass accuracy, ppm negative mode
		$[M + H]^+$	$[M + HCOO]^-$		
Sphingomyelin	SM 32:1:1		719.5348		0.43
	SM 33:1:1	689.5592	733.5500	0.04	-0.23
	SM 34:1:1	703.5749	747.5658	0.05	-0.03
	SM 34:2:1	701.5592	745.5494	-0.02	-1.02
	SM 35:1:1	717.5906	761.5819	0.07	0.68
	SM 36:1:1	731.6063	775.5966	0.14	-0.66
	SM 36:2:1	729.5906	773.5807	0.16	-0.95
	SM 37:1:1	745.6219	789.6111	0.10	-2.04
	SM 38:1:1	759.6375	803.6271	0.02	-1.57
	SM 38:2:1		801.6124		-0.37
	SM 39:1:1	773.6532	817.6424	0.08	-1.94
	SM 40:1:1	787.6689	831.6585	0.16	-1.46
	SM 40:2:1	785.6533	829.6432	0.28	-0.95
	SM 41:1:1	801.6846	845.6742	0.26	-1.30
	SM 41:2:1	799.6689	843.6586	0.24	-1.29
	SM 42:1:1	815.7004	859.6899	0.37	-1.20
	SM 42:2:1	813.6847	857.6743	0.35	-1.16
	SM 42:3:1	811.6691	855.6588	0.38	-1.07
	SM 43:1:1	829.7171	873.7062	1.69	-0.54
	SM 43:2:1		871.6902		-0.90
		$[M + H]^+$	$[M - H]^-$		
3-sn-phosphatidyl-ethanolamine	PE 34:0	720.5538	718.5392	0.06	-0.03
	PE 34:1	718.5380	716.5237	-0.21	0.14
	PE 34:2	716.5226	714.5080	0.20	0.12
	PE 34:3		712.4924		0.17
	PE 35:1		730.5387		-0.72
	PE 35:2		728.5235		-0.14
	PE 36:0	748.5849		-0.30	
	PE 36:1	746.5694	744.5542	0.03	-0.95
	PE 36:2	744.5533	742.5392	-0.60	-0.10
	PE 36:3	742.5385	740.5236	0.56	0.06
	PE 36:4	740.5221	738.5080	-0.57	0.08
	PE 36:5		736.4922		-0.10
	PE 37:1		758.5707		0.21
	PE 37:2		756.5551		0.33
	PE 37:3		754.5389		-0.39
	PE 37:4		752.5236		0.02
	PE 38:1	774.6007	772.5853	0.02	-1.19
	PE 38:2	772.5845	770.5692	-0.75	-1.73
	PE 38:4	768.5537	766.5390	-0.12	-0.36
	PE 38:5	766.5376	764.5239	-0.67	0.41
	PE 38:6	764.5226	762.5086	0.19	0.88
	PE 39:2		784.5860		-0.21
	PE 39:3		782.5705		-0.04
	PE 39:4		780.5556		0.87

Lipid class	Lipid species	*m/z* *		Mass accuracy, ppm	
		positive mode	negative mode	positive mode	negative mode
	PE 40:3	798.6008	796.5851	0.07	-1.34
	PE 40:4	796.5853	794.5694	0.24	-1.46
	PE 40:5	794.5697	792.5539	0.29	-1.21
	PE 40:6	792.5535	790.5388	-0.40	-0.56
		$[M + H]^+$	$[M - H]^-$		
Plasmenyl- and plasmanylphosphatidyl-ethanolamine	PE-O 32:1		674.5127		-0.44
	PE-O 32:2		672.4971		-0.43
	PE-O 33:2		686.5129		-0.19
	PE-O 33:3		684.4972		-0.18
	PE-O 34:1	704.5587	702.5440	-0.22	-0.48
	PE-O 34:2	702.5432	700.5281	-0.04	-0.77
	PE-O 34:3	700.5276	698.5128	0.05	-0.26
	PE-O 34:4	698.5119	696.4974	0.04	0.07
	PE-O 34:5		694.4817		0.05
	PE-O 35:1		716.5595		-0.61
	PE-O 35:2		714.5442		-0.11
	PE-O 35:3		712.5286		-0.08
	PE-O 35:4		710.5130		-0.08
	PE-O 35:5		708.4973		-0.16
	PE-O 36:1	732.5898	730.5749	-0.45	-0.91
	PE-O 36:2	730.5745	728.5583	-0.02	-2.24
	PE-O 36:3	728.5589	726.5439	0.07	-0.62
	PE-O 36:4	726.5433	724.5284	0.16	-0.39
	PE-O 36:5	724.5277	722.5131	0.20	0.10
	PE-O 36:6		720.4977		0.40
	PE-O 37:3		740.5599		-0.11
	PE-O 37:4		738.5436		-0.93
	PE-O 37:5		736.5286		-0.12
	PE-O 37:6		734.5129		-0.17
	PE-O 38:2	758.6056		-0.33	
	PE-O 38:3	756.5903	754.5747	0.14	-1.18
	PE-O 38:4	754.5746	752.5591	0.06	-1.16
	PE-O 38:5	752.5589	750.5439	0.11	-0.59
	PE-O 38:6	750.5433	748.5285	0.07	-0.28
	PE-O 38:7		746.5131		0.12
	PE-O 39:5		764.5606		0.79
	PE-O 39:6		762.5451		1.00
	PE-O 40:4	782.6058	780.5909	-0.07	-0.47
	PE-O 40:5	780.5902	778.5745	0.09	-1.43
	PE-O 40:6	778.5746	776.5591	0.12	-1.12
	PE-O 40:7	776.5582	774.5441	-0.87	-0.23

Lipid class	Lipid species	*m/z* *		Mass accuracy, ppm	
		positive mode	negative mode	positive mode	negative mode
		$[M + H]^+$	$[M - H]^-$		
Lysophosphatidyl-ethanolamine	LPE 16:0		452.2785		0.58
	LPE 17:0		466.2943		0.93
	LPE 18:0	482.3239	480.3097	-0.41	0.33
	LPE 18:1	480.3083	478.2942	-0.41	0.68
	LPE 18:2	478.2926	476.2785	-0.38	0.57
	LPE 20:3		502.2942		0.65
	LPE 20:4	502.2926	500.2785	-0.42	0.54
	LPE 20:5		498.2631		0.90
	LPE 22:4		528.3101	1.05	1.05
	LPE 22:5		526.2945		1.17
		$[M + H]^+$	$[M + HCOO]^-$		
3-sn-phosphatidyl-choline	PC 30:0	706.5382	750.5285	0.07	-0.70
	PC 31:0		764.5449		0.30
	PC 32:0	734.5696	778.5597	0.17	-0.90
	PC 32:1	732.5539	776.5441	0.16	-0.73
	PC 33:1		790.5593		-1.29
	PC 33:0		792.5748		-1.49
	PC 34:2	758.5693	802.5597	-0.17	-0.87
	PC 34:3		800.5447		-0.05
	PC 34:4		798.5297		0.84
	PC 35:0		820.6065		-1.01
	PC 35:1		818.5902		-1.77
	PC 35:2		816.5748		-1.54
	PC 36:0	790.6319	834.6213	-0.17	-1.96
	PC 36:1	788.6164	832.6059	-0.01	-1.71
	PC 36:2	786.5996	830.5904	-1.43	-1.57
	PC 36:3		828.5747		-1.56
	PC 36:4	782.5694	826.5594	-0.10	-1.19
	PC 36:5		824.5440		-0.86
	PC 37:0		848.6379		-0.80
	PC 37:1		846.6219		-1.22
	PC 37:2		844.6062		-1.36
	PC 37:3		842.5906		-1.29
	PC 37:4		840.5749		-1.38
	PC 38:1	816.6478	860.6378	0.15	-0.94
	PC 38:2	814.6326	858.6223	0.66	-0.80
	PC 38:3	812.6165	856.6062	0.20	-1.27
	PC 38:4	810.6009	854.5904	0.27	-1.53
	PC 38:5	808.5852	852.5751	0.13	-1.09
	PC 38:6	806.5695	850.5596	0.13	-0.92
	PC 39:1		874.6536		-0.74
	PC 39:2		872.6379		-0.85
	PC 39:3		870.6213		-1.92
	PC 39:4		868.6061		-1.34
	PC 40:4	838.6324	882.6225	0.43	-0.52

Lipid class	Lipid species	*m/z* *		Mass accuracy, ppm	
		positive mode	negative mode	positive mode	negative mode
	PC 40:5	836.6167	880.6067	0.34	-0.73
	PC 40:6		878.5909		-0.85
	PC 40:7	832.5841	876.5758	-1.13	-0.25
		$[M + H]^+$	$[M + HCOO]^-$		
Plasmenyl- and plasmanylphosphatidyl-choline	PC-O 30:1	690.5432	734.5340	0.02	-0.14
	PC-O 31:1		748.5491		-0.98
	PC-O 31:2		746.5348		0.89
	PC-O 32:1	718.5746	762.5660	0.10	0.76
	PC-O 32:2	716.5587	760.5502	-0.19	0.54
	PC-O 32:3	714.5432	758.5344	0.04	0.33
	PC-O 33:2		774.5646		-1.04
	PC-O 33:3		772.5493		-0.67
	PC-O 33:4		770.5336		-0.76
	PC-O 34:3	742.5743	786.5650	-0.23	-0.53
	PC-O 34:4	740.5577	784.5497	-1.52	-0.06
	PC-O 34:5	738.5434	782.5342	0.27	0.06
	PC-O 35:3		800.5806		-0.63
	PC-O 35:4		798.5651		-0.46
	PC-O 35:5		796.5499		0.10
	PC-O 36:3	770.6057	814.5952	-0.15	-1.95
	PC-O 36:4	768.5900	812.5795	-0.28	-1.98
	PC-O 36:5	766.5744	810.5642	-0.12	-1.51
	PC-O 36:6	764.5572	808.5486	-2.14	-1.43
	PC-O 37:4		826.5956		-1.34
	PC-O 37:5		824.5803		-0.94
	PC-O 37:6		822.5653		-0.22
	PC-O 38:4	796.6215	840.6110	-0.01	-1.71
	PC-O 38:5	794.6059	838.5954	0.11	-1.64
	PC-O 38:6	792.5902	836.5798	0.09	-1.60
	PC-O 38:7		834.5644		-1.22
	PC-O 39:5		852.6116		-0.88
	PC-O 39:6		850.5960		-0.86
	PC-O 40:5	822.6376	866.6271	0.59	-1.04
	PC-O 40:6	820.6218	864.6114	0.39	-1.13
	PC-O 40:7	818.6058	862.5959	0.01	-1.01
		$[M + H]^+$	$[M + HCOO]^-$		
Lysophosphatidyl-choline	LPC 16:0	496.3395	540.3308	-0.47	0.24
	LPC 16:1		538.3153		0.39
	LPC 17:0		554.3465		0.20
	LPC 18:0	524.3709	568.3621	-0.30	0.24
	LPC 18:1	522.3552	566.3464	-0.44	0.16
	LPC 18:2	520.3395	564.3308	-0.53	0.26
	LPC 18:3		562.3154		0.56
	LPC 20:3	546.3553	590.3465	-0.18	0.30
	LPC 20:4	544.3397	588.3308	-0.18	0.26
	LPC 22:4		616.3621		0.14

Lipid class	Lipid species	*m/z* * positive mode	*m/z* * negative mode	Mass accuracy, ppm positive mode	Mass accuracy, ppm negative mode
	LPC 22:5		614.3466		0.38
		$[M + H]^+$	$[M - H]^-$		
3-sn-phosphatidyl-serine	PS 36:2	788.5438	786.5310	0.26	2.41
	PS 36:3		784.5128		-0.76
		$[M + NH_4]^+$	$[M - H]^-$		
1-phosphatidylinositol	PI 35:1		849.5488		-1.28
	PI 35:2		847.5345		0.32
	PI 36:1	882.6064	863.5641	-0.22	-1.59
	PI 36:2	880.5910	861.5486	0.05	-1.45
	PI 36:3	878.5762	859.5334	0.99	-0.92
	PI 36:4		857.5179		-0.76
	PI 37:1		877.5798		-1.60
	PI 37:2		875.5635		-2.26
	PI 37:3		873.5491		-0.84
	PI 37:4		871.5326		-1.80
	PI 38:2		889.5817		0.57
	PI 38:3	906.6062	887.5641	-0.41	-1.57
	PI 38:4	904.5910	885.5487	0.05	-1.25
	PI 38:5	902.5757	883.5335	0.39	-0.83
	PI 38:6		881.5185		-0.07
	PI 40:4	932.6222	913.5793	-0.09	-1.98
	PI 40:5	930.6065	911.5638	-0.07	-1.88
	PI 40:6		909.5484		-1.64
			$[M - H]^-$		
Lysophosphatidylinositol	LPI 18:0		599.3203		0.18
			$[M - 2H]^-$		
Cardiolipin	CL 70:6		711.4790		-0.37
	CL 70:7		710.4712		-0.59
	CL 72:7		724.4858		2.29
	CL 72:8		723.4788		0.01
	CL 72:9		722.4709		0.29
			$[M - H]^-$		
Monolysocardiolipin	mLCL 52:4		1159.7192		-0.35
	mLCL 52:3		1161.7353		0.01
	mLCL 54:5		1185.7349		-0.33
			$[M - H]^-$		
Dilysocardiolipin	dLCL 36:4		923.5042		-1.53
			$[M - H]^-$		
3-sn-phosphatidyl-glycerol	PG 32:0		721.5009		-2.22
	PG 34:0		749.532		-2.39
	PG 34:1		747.5182		0.01
	PG 34:2		745.5027		0.23
	PG 35:1		761.5344		0.73
	PG 36:1		775.5486		-1.13
	PG 36:2		773.5334		-0.58
	PG 36:3		771.5172		-1.20

Lipid class	Lipid species	*m/z* *		Mass accuracy, ppm	
		positive mode	negative mode	positive mode	negative mode
	PG 36:4		769.5017		-1.09
	PG 38:4		797.5335		-0.44

* - *m/z* averaged over 10 independent experiments on the same bovine heart extract

Table S2. Average concentrations of lipid species in human blood plasma of 10 individuals. Each total extract was analyzed twice by successive acquisition of FT MS(+) and FT MS(-) spectra.

Lipid class	Lipid species	*m/z* *		Mass accuracy, ppm		Average concentration #, μM	Standard deviation, μM
		positive mode	negative mode	positive mode	negative mode		
		$[M + NH_4]^+$					
Cholesterol	Chol	404.3886		-0.23		1334.80	284.99
		$[M + NH_4]^+$					
Cholesteryl ester	CholE 14:0	614.5871		0.08		30.76	12.34
	CholE 15:0	628.6029		0.29		7.89	2.83
	CholE 16:0	642.6186		0.41		421.98	104.35
	CholE 16:1	640.6030		0.45		182.87	88.99
	CholE 17:0	656.6354		2.12		6.74	3.02
	CholE 17:1	654.6186		0.35		12.43	3.99
	CholE 18:0	670.6490		-0.98		19.22	8.05
	CholE 18:1	668.6336		-0.60		929.52	227.71
	CholE 18:2	666.6183		-0.03		3086.02	693.79
	CholE 18:3	664.6028		0.11		122.10	34.13
	CholE 19:2	680.6329		-1.59		10.52	6.95
	CholE 20:2	694.6490		-0.89		3.57	1.66
	CholE 20:3	692.6336		-0.53		54.82	18.06
	CholE 20:4	690.6182		-0.23		547.73	191.99
	CholE 20:5	688.6025		-0.24		87.14	51.94
	CholE 22:5	716.6338		-0.31		2.64	1.45
	CholE 22:6	714.6183		-0.01		50.35	25.89

Lipid class	Lipid species	*m/z* *		Mass accuracy, ppm		Average concentration #, µM	Standard deviation, µM
		positive mode	negative mode	positive mode	negative mode		
		$[M + NH_4]^+$	$[M + HCOO]^-$				
Triacylglycerol	TAG 44:0	768.7074		-0.18		2.23	2.96
	TAG 44:1	766.6923		0.54		2.86	3.53
	TAG 46:1	794.7230		-0.24		8.66	7.75
	TAG 46:2	792.7073		-0.38		3.49	3.73
	TAG 46:3	790.6919		-0.07		0.97	1.04
	TAG 47:1	808.7387		-0.23		1.76	1.95
	TAG 48:1	822.7543		-0.24		24.69	26.62
	TAG 48:2	820.7387		-0.20		18.13	17.17
	TAG 48:3	818.7231		-0.19		5.41	4.28
	TAG 49:1	836.7700		-0.20		3.32	3.38
	TAG 49:2	834.7544		-0.09		2.53	2.03
	TAG 49:3	832.7391		0.34		1.37	0.51
	TAG 50:1	850.7855		-0.36		54.23	56.61
	TAG 50:2	848.7700	875.7348	-0.22	0.25	75.78	64.58
	TAG 50:3	846.7544		-0.15		32.90	25.05
	TAG 50:4	844.7388		-0.09		7.88	5.29
	TAG 50:5	842.7232		-0.04		1.36	0.88
	TAG 51:1	864.8011		-0.37		2.33	2.61
	TAG 51:2	862.7857		-0.09		5.92	4.73
	TAG 51:3	860.7701		-0.05		3.33	2.11
	TAG 51:4	858.7545		-0.03		0.91	0.61
	TAG 52:2	876.8010	903.7661	-0.54	0.28	158.98	115.36
	TAG 52:3	874.7856	901.7504	-0.28	0.18	138.33	83.95
	TAG 52:4	872.7700	899.7348	-0.13	0.29	54.12	31.47
	TAG 52:5	870.7546		0.09		12.34	7.36
	TAG 52:6	868.7387		-0.16		2.41	1.32
	TAG 53:2	890.8169		-0.21		2.74	2.02
	TAG 53:3	888.8013		-0.20		2.98	1.86
	TAG 53:4	886.7858		-0.06		1.14	0.88

Lipid class	Lipid species	*m/z* *		Mass accuracy, ppm		Average concentration #, µM	Standard deviation, µM
		positive mode	negative mode	positive mode	negative mode		
Triacylglycerol	TAG 53:5	884.7697		-0.50		0.47	0.37
	TAG 54:2	904.8303		-2.69		3.83	4.54
	TAG 54:3	902.8169	929.7818	-0.26	0.36	39.94	27.36
	TAG 54:4	900.8013	927.7660	-0.22	0.19	35.94	22.67
	TAG 54:5	898.7856		-0.20		24.45	14.91
	TAG 54:6	896.7700		-0.18		11.72	6.58
	TAG 54:7	894.7543		-0.23		3.66	2.17
	TAG 54:8	892.7386		-0.34		0.49	0.49
	TAG 56:2	932.8630		-1.13		0.64	0.51
	TAG 56:3	930.8482		-0.25		1.03	0.89
	TAG 56:5	926.8170		-0.12		5.46	3.56
	TAG 56:6	924.8013		-0.17		8.68	5.26
	TAG 56:7	922.7856		-0.18		9.46	6.60
	TAG 56:8	920.7700		-0.17		4.13	3.04
	TAG 56:9	918.7543		-0.21		0.72	0.67
	TAG 58:5	954.8484		0.03		0.55	0.30
	TAG 58:6	952.8327		-0.10		0.68	0.54
	TAG 58:7	950.8169		-0.19		1.43	1.08
	TAG 58:8	948.8012		-0.25		2.06	2.00
	TAG 58:9	946.7855		-0.33		1.34	1.35
	TAG 58:10	944.7697		-0.52		1.73	1.61
		$[M + NH_4]^+$	$[M + HCOO]^-$				
Diacylglycerol	DAG 32:1	584.5249	611.4895	0.11	0.39	1.67	1.56
	DAG 32:2		609.4736		0.07	0.72	0.63
	DAG 34:1	612.5562	639.5208	0.11	0.45	6.07	5.09
	DAG 34:2	610.5405	637.5052	0.08	0.43	3.86	3.40
	DAG 34:3		635.4895		0.43	0.85	0.77
	DAG 34:4	606.5092	633.4730	0.03	-0.86	1.37	0.71
	DAG 36:1		667.5523		0.68	1.02	0.92

Lipid class	Lipid species	*m/z* *		Mass accuracy, ppm		Average concentration #, µM	Standard deviation, µM
		positive mode	negative mode	positive mode	negative mode		
	DAG 36:2	638.5721	665.5367	0.44	0.73	9.32	5.97
	DAG 36:3	636.5564	663.5210	0.38	0.77	6.24	3.83
	DAG 36:4		661.5053		0.65	2.21	1.33
	DAG 38:5		687.5209		0.55	1.28	0.80
	DAG 38:6		685.5055		0.91	0.66	0.59
	DAG 40:8		709.5057		1.14	1.31	0.61
		$[M + H]^+$	$[M + HCOO]^-$				
Ceramide	Cer 34:1:1		582.5105		0.33	0.24	0.07
	Cer 36:1:1		610.5418		0.36	0.12	0.05
	Cer 38:1:1		638.5732		0.42	0.10	0.06
	Cer 40:1:1		666.6047		0.68	0.50	0.15
	Cer 41:1:1		680.6202		0.54	0.48	0.20
	Cer 42:1:1	650.6449	694.6357	0.53	0.24	1.76	0.53
	Cer 42:2:1	648.6292	692.6201	0.45	0.29	1.15	0.38
	Cer 43:1:1		708.6514		0.39	0.19	0.10
		$[M + H]^+$	$[M + HCOO]^-$				
Sphingomyelin	SM 32:1:1	675.5434	719.5349	-0.21	0.56	10.05	3.04
	SM 32:2:1	673.5280	717.5196	0.17	1.03	0.59	0.25
	SM 33:1:1	689.5587	733.5507	-0.69	0.74	4.65	1.41
	SM 34:1:1	703.5748	747.5664	-0.06	0.78	100.96	18.92
	SM 34:2:1	701.5592	745.5508	-0.03	0.88	12.73	3.03
	SM 35:1:1	717.5905	761.5820	0.05	0.69	1.90	0.52
	SM 36:1:1	731.6064	775.5978	0.33	0.92	15.42	4.51
	SM 36:2:1	729.5908	773.5821	0.37	0.89	6.72	1.74
	SM 36:3:1	727.5750	771.5647	0.27	-1.34	0.31	0.11
	SM 37:1:1	745.6219	789.6137	0.17	1.24	0.90	0.45
	SM 38:1:1	759.6377	803.6291	0.31	0.92	10.38	3.18
	SM 38:2:1	757.6222	801.6139	0.59	1.44	3.88	0.98
	SM 39:1:1	773.6532	817.6444	0.09	0.43	3.54	1.30

Lipid class	Lipid species	*m/z* *		Mass accuracy, ppm		Average concentration [#], µM	Standard deviation, µM
		positive mode	negative mode	positive mode	negative mode		
	SM 39:2:1	771.6379	815.6287	0.62	0.34	0.58	0.24
	SM 40:1:1	787.6688	831.6598	0.04	0.14	20.88	6.80
	SM 40:2:1	785.6523	829.6444	-1.00	0.43	18.77	5.56
	SM 40:3:1	783.6378	827.6288	0.42	0.49	1.18	0.46
	SM 41:1:1	801.6846	845.6745	0.23	-0.96	4.43	1.78
	SM 41:2:1	799.6686	843.6571	-0.16	-3.08	4.85	2.13
	SM 41:3:1	797.6535	841.6437	0.46	-0.34	0.77	0.45
	SM 42:1:1	815.7000	859.6908	-0.05	-0.19	13.03	4.89
	SM 42:1:2	831.6951	875.6862	0.21	0.38	1.29	0.69
	SM 42:2:1	813.6845	857.6755	0.16	0.23	58.59	17.76
	SM 42:3:1	811.6689	855.6599	0.20	0.27	26.65	8.00
	SM 42:4:1	809.6526	853.6443	-0.60	0.37	1.80	0.58
	SM 43:1:1	829.7163	873.7060	0.76	-0.67	0.41	0.23
	SM 43:2:1	827.7007	871.6913	0.76	0.32	1.93	0.79
		$[M + H]^+$	$[M - H]^-$				
3-sn-phosphatidyl-ethanolamine	PE 34:1		716.5239		0.47	1.16	1.28
	PE 34:2		714.5083		0.49	2.40	2.67
	PE 36:1		744.5555		0.83	0.85	0.75
	PE 36:2		742.5398		0.76	5.42	4.64
	PE 36:3		740.5241		0.66	1.39	1.56
	PE 36:4		738.5085		0.74	3.03	2.76
	PE 38:3		768.5549		0.03	0.62	0.40
	PE 38:4		766.5398		0.68	6.11	4.06
	PE 38:5		764.5241		0.63	1.84	1.46
	PE 38:6		762.5084		0.60	4.57	5.16
	PE 40:6		790.5402		1.25	2.18	2.11

Lipid class	Lipid species	*m/z* *		Mass accuracy, ppm		Average concentration [#], µM	Standard deviation, µM
		positive mode	negative mode	positive mode	negative mode		
		$[M + H]^+$	$[M - H]^-$				
Plasmenyl- and plasmanylphosphatidyl-ethanolamine	PE-O 34:2		700.5289		0.27	0.62	0.22
	PE-O 34:3		698.5133		0.36	1.02	0.45
	PE-O 36:2		728.5604		0.64	0.54	0.19
	PE-O 36:3	728.5588	726.5447	-0.02	0.57	1.85	0.61
	PE-O 36:4		724.5292		0.76	1.64	0.70
	PE-O 36:5		722.5134		0.52	3.97	1.31
	PE-O 38:4		752.5602		0.30	0.75	0.28
	PE-O 38:5		750.5446		0.40	6.01	2.01
	PE-O 38:6	750.5436	748.5291	0.54	0.59	5.22	1.70
	PE-O 38:7	748.5278	746.5136	0.37	0.79	2.83	1.28
	PE-O 40:5		778.5757		0.12	0.34	0.11
	PE-O 40:6		776.5599		-0.12	0.70	0.33
	PE-O 40:7		774.5448		0.65	1.95	0.81
	PE-O 40:8		772.5293		0.81	1.03	0.60
	PE-O 42:6		804.5898		-1.82	0.77	0.38
	PE-O 42:7		802.5762		0.71	1.31	0.63
		$[M + H]^+$	$[M - H]^-$				
Lysophosphatidyl-ethanolamine	LPE 16:0		452.2784		0.40	1.99	0.75
	LPE 18:0		480.3097		0.37	3.82	1.07
	LPE 18:1		478.2941		0.34	1.65	0.54
	LPE 18:2		476.2785		0.42	3.56	1.21
	LPE 20:2		504.3098		0.50	0.36	0.16
	LPE 20:4		500.2786		0.66	2.83	1.03
	LPE 22:6		524.2787		0.79	1.94	0.76

Lipid class	Lipid species	*m/z* *		Mass accuracy, ppm		Average concentration [#], µM	Standard deviation, µM
		positive mode	negative mode	positive mode	negative mode		
		$[M + H]^+$	$[M + HCOO]^-$				
3-sn-phosphatidyl-choline	PC 30:0	706.5381	750.5293	0.02	0.39	3.68	2.39
	PC 32:0	734.5697	778.5609	0.30	0.69	12.73	4.79
	PC 32:1	732.5540	776.5453	0.31	0.78	21.63	14.68
	PC 32:2	730.5382	774.5298	0.03	0.91	4.31	2.63
	PC 33:1		790.5614		1.26	3.93	1.32
	PC 33:2		788.5457		1.22	1.07	0.54
	PC 34:1	760.5849	804.5760	-0.28	0.02	291.32	95.86
	PC 34:2	758.5696	802.5613	0.24	1.16	556.27	187.56
	PC 34:3	756.5541	800.5458	0.49	1.42	17.06	7.81
	PC 34:4	754.5386	798.5302	0.62	1.45	1.33	0.89
	PC 35:1		818.5919		0.31	4.27	1.09
	PC 35:2		816.5763		0.33	10.09	2.79
	PC 35:3		814.5607		0.41	0.41	0.21
	PC 36:1	788.6158	832.6061	-0.69	-1.43	50.29	16.57
	PC 36:2	786.6006	830.5918	-0.15	0.17	298.67	56.43
	PC 36:3	784.5849	828.5761	-0.22	0.14	174.87	44.12
	PC 36:4	782.5693	826.5608	-0.20	0.57	262.59	102.33
	PC 36:5		824.5453		0.66	30.90	16.39
	PC 37:2		844.6072		-0.10	0.99	0.41
	PC 37:3		842.5917		0.07	2.13	0.73
	PC 37:4		840.5763		0.31	4.65	2.60
	PC 38:3	812.6163	856.6073	-0.12	-0.02	47.44	14.57
	PC 38:4	810.6007	854.5923	0.02	0.79	149.76	60.81
	PC 38:5	808.5847	852.5761	-0.51	0.08	67.61	22.36
	PC 38:6	806.5694	850.5602	-0.01	-0.16	36.45	21.83
	PC 38:7		848.5454		0.83	1.62	0.75
	PC 39:6		864.5774		1.65	1.04	1.12
	PC 40:4		882.6234		0.49	2.59	0.86
	PC 40:5	836.6159	880.6072	-0.58	-0.13	9.61	3.16

Lipid class	Lipid species	*m/z* *		Mass accuracy, ppm		Average concentration #, µM	Standard deviation, µM
		positive mode	negative mode	positive mode	negative mode		
	PC 40:6	834.6005	878.5918	-0.31	0.12	33.50	18.86
	PC 40:7		876.5762		0.16	5.88	3.20
		$[M + H]^+$	$[M + HCOO]^-$				
Plasmenyl- and plasmanylphosphatidyl-choline	PC-O 32:0	720.5903	764.5816	0.15	0.65	1.46	0.57
	PC-O 32:1	718.5747	762.5660	0.19	0.71	1.55	0.68
	PC-O 34:1	746.6062	790.5977	0.52	1.20	3.77	1.00
	PC-O 34:2	744.5905	788.5820	0.48	1.16	6.20	1.73
	PC-O 34:3	742.5745	786.5663	0.04	1.14	5.42	1.43
	PC-O 36:2	772.6215	816.6126	0.04	0.31	1.71	0.68
	PC-O 36:3	770.6058	814.5969	-0.07	0.17	4.42	1.04
	PC-O 36:4	768.5903	812.5814	0.11	0.34	12.96	2.99
	PC-O 36:5	766.5746	810.5658	0.07	0.39	7.91	2.03
	PC-O 38:4	796.6215	840.6125	0.00	0.10	6.64	1.70
	PC-O 38:5	794.6059	838.5969	0.09	0.24	14.20	3.97
	PC-O 38:6	792.5904	836.5813	0.29	0.20	5.13	1.66
	PC-O 38:7	790.5740	834.5661	-0.70	0.74	1.13	0.60
	PC-O 40:7	818.6061	862.5975	0.34	0.87	1.75	1.00
		$[M + H]^+$	$[M + HCOO]^-$				
Lysophosphatidyl-choline	LPC 14:0	468.3085	512.2997	0.00	0.56	3.27	1.26
	LPC 15:0		526.3154		0.74	1.21	0.31
	LPC 16:0	496.3397	540.3309	-0.05	0.38	185.80	54.27
	LPC 16:1	494.3241	538.3151	0.00	0.18	5.01	1.73
	LPC 17:0		554.3465		0.33	2.34	0.80
	LPC 18:0	524.3709	568.3623	-0.23	0.50	50.53	16.01
	LPC 18:1	522.3554	566.3466	-0.09	0.52	42.39	13.56
	LPC 18:2	520.3394	564.3311	-0.69	0.63	55.61	15.14
	LPC 18:3		562.3153		0.54	0.75	0.37
	LPC 20:3	546.3562	590.3466	1.48	0.35	3.62	1.16
	LPC 20:4	544.3400	588.3309	0.49	0.43	11.70	5.16

Lipid class	Lipid species	*m/z* * positive mode	*m/z* * negative mode	Mass accuracy, ppm positive mode	Mass accuracy, ppm negative mode	Average concentration #, µM	Standard deviation, µM
	LPC 20:5		586.3152	-0.10	0.33	1.30	1.06
	LPC 22:6	568.3401	612.3308	0.51	0.12	2.17	1.23
		$[M + H]^+$	$[M + HCOO]^-$				
Lysoplasmenyl- and lysoplasmanyl-phosphatidylcholine	LPC-O 16:0	482.3605	526.3518	-0.06	0.75	0.60	0.26
	LPC-O 16:1	480.3449	524.3360	0.08	0.45	0.64	0.35
	LPC-O 18:1	508.3761	552.3672	-0.09	0.19	0.46	0.24
		$[M + NH_4]^+$	$[M - H]^-$				
1-phosphatidylinositol	PI 34:1		835.5348		0.69	3.87	2.34
	PI 34:2	852.5605	833.5190	0.96	0.48	2.66	1.80
	PI 36:1		863.5655		0.04	3.86	1.66
	PI 36:2	880.5915	861.5500	0.65	0.17	10.91	5.99
	PI 36:3	878.5768	859.5346	1.75	0.48	1.63	0.59
	PI 36:4		857.5188		0.32	3.52	1.81
	PI 38:4	904.5915	885.5498	0.59	-0.04	36.83	14.59
	PI 40:6		909.5489		-1.07	1.43	1.01
		$[M + H]^+$	$[M - H]^-$				
3-sn-phosphatidyl-serine	PS 36:1		788.5457		1.22	1.14	0.57
	PS 38:2		814.5607		0.41	0.19	0.09
	PS 38:3		812.5444		0.94	0.40	0.20

* - *m/z* averaged over 20 independent experiments (10 plasma samples measured in 2 replicates)
# - concentration averaged over of 20 experiments performed on 10 plasma samples

Note: In a few instances monoisotopic peaks of lipid species might have overlapped with the second isotopic peak of the same class species, but having additional double bond in a hydrocarbon moiety (fatty acid, fatty alcohol) – for example, as TAG 50:0 and TAG 50:1. At the $R_{m/z\ 400}$ = 100,000 these peaks were not resolved. In these instances we compared the relative abundance of second isotope peak with its abundance expected from the isotopic distribution. More saturated species were only reported and quantified using isotopic correction algorithm of LipidXplorer if the isotope abundance difference exceeded the factor of two. Therefore it is likely that some low abundant species were missed, although this might have only minor impact on the total profile of species of each lipid class and distribution of corresponding fatty acid / fatty alcohol moieties.